



UNIVERSITY OF THESSALY
SCHOOL OF ENGINEERING
DEPARTMENT OF ELECTRICAL AND COMPUTER ENGINEERING

GERMANIUM (Ge) FOR MICROELECTRONIC APPLICATIONS

Diploma Thesis

Makropoulou Paraskevi

Supervisor: Chroneos Alexandros

October 2023



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ΠΑΝΕΠΙΣΤΗΜΙΟ ΘΕΣΣΑΛΙΑΣ

ΠΟΛΥΤΕΧΝΙΚΗ ΣΧΟΛΗ

ΤΜΗΜΑ ΗΛΕΚΤΡΟΛΟΓΩΝ ΜΗΧΑΝΙΚΩΝ ΚΑΙ ΜΗΧΑΝΙΚΩΝ ΥΠΟΛΟΓΙΣΤΩΝ

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Makropoulou Paraskevi

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Makropoulou Paraskevi

Abstract

In 1947 the state of the art invention of the transistor took place at Bell Laboratories. Three prominent scientists William Shockley, Walter Brattain and John Bardeen fabricated the first transistor which was made of Germanium (Ge) with two gold foil contacts placed on the crystal. This was the device that substituted the vacuum tubes. Despite the first transistor was made out of Ge crystal, Si soon substituted Ge and dominated the electronics' industry up to date. However, during the last years and as we are approaching towards the physical limits concerning the size of the Si transistors, scientists are investigating new materials to continue growing the computing power of our devices while at the same time keep decreasing their cost. One of the materials that are under investigation is Ge which we are going to analyze in this thesis. We will start by describing the doping behaviour in Ge as well as the diffusion of the carriers in it. Besides, we are going to refer to the evolution of the transistor during the first years and how Ge was substituted by Si. Furthermore, we are going to analyze the applications of Ge today including infrared imaging, infrared detection and photovoltaics and we are going to conclude with deeply describing Moore's law and its physical limitations which are the main reason scientists are experimenting with new channel materials in MOSFETs. The main goal of this thesis is to find out if there is a possibility of Ge dominating the semiconductors industry after decades of being overshadowed by Si.

Keywords:

Germanium, Silicon, Semiconductors, transistor, n-type doping, p-type doping, Diffusion, Moore's law, Ge MOSFET, infrared detection, infrared imaging

Διπλωματική Εργασία

ΓΕΡΜΑΝΙΟ (Ge) ΓΙΑ ΜΙΚΡΟΗΛΕΚΤΡΟΝΙΚΕΣ ΕΦΑΡΜΟΓΕΣ

Μακροπούλου Παρασκευή

Περίληψη

Το 1947 στο εργαστήριο της εταιρίας Bell Laboratories ανακαλύφθηκε το πρώτο τρανζίστορ. Τρεις διακεκριμένοι επιστήμονες οι William Shockley, Walter Brattain και John Bardeen κατασκεύασαν το πρώτο τρανζίστορ χρησιμοποιώντας ημιαγωγό Γερμανίου στον οποίο τοποθέτησαν ηλεκτρόδια χρυσού. Το τρανζίστορ ήταν αυτό που αντικατέστησε τις δύσχρηστες λυχνίες κενού στους υπολογιστές. Αν και το πρώτο τρανζίστορ αποτελούνταν από ημιαγωγό Γερμανίου, το Πυρίτιο αντικατέστησε σύντομα το Γερμάνιο και κατέλαβε την βιομηχανία ηλεκτρονικών μέχρι και σήμερα. Ωστόσο, τα τελευταία χρόνια και καθώς πλησιάζουμε τα φυσικά όρια όσον αφορά το μέγεθος των τρανζίστορ Πυριτίου, οι επιστήμονες διερευνούν ποια ημιαγωγικά υλικά μπορούν να αντικαταστήσουν το Πυρίτιο ώστε να συνεχιστεί να αυξάνεται η επεξεργαστική ισχύς των ηλεκτρονικών μας συσκευών ενώ την ίδια ώρα μειώνεται το κόστος τους. Ένα από τα ημιαγωγικά υλικά που είναι υπο διερεύνηση είναι και το Γερμάνιο με το οποίο θα ασχοληθούμε στην παρούσα εργασία. Θα ξεκινήσουμε αναλύοντας την διαδικασία νόθευσης του Γερμανίου όπως επίσης και την διάχυση των φορέων σε αυτό για να καταλάβουμε τα προτερήματα και τα μειονεκτήματα της χρήσης του στην βιομηχανία ημιαγωγών. Κατόπιν, θα αναφερθούμε στην εξέλιξη του τρανζίστορ τα πρώτα χρόνια μετά την ανακάλυψη του και θα αναλύσουμε τις κύριες κατηγορίες των τρανζίστορ που κατασκευάζονται μέχρι και σήμερα. Θα περιγράψουμε επίσης κάποιες από τις κύριες χρήσεις του Γερμανίου σήμερα όπως τα φωτοβολταϊκά, η ανίχνευση υπέρυθρων ακτινοβολιών κτλ. Τέλος θα αναλύσουμε τις προκλήσεις που αντιμετωπίζει σήμερα η βιομηχανία ημιαγωγών με κύριο άξονα τον νόμο του Moore και την δυνατότητα η μη συνέχισης του και την πιθανότητα να είναι το Γερμάνιο ένα από τα υλικά που θα αντικαταστήσει το Πυρίτιο για την κατασκευή του δομικού λίθου των ολοκληρωμένων κύκλωμάτων -το τρανζίστορ-.

Λέξεις-κλειδιά:

Γερμάνιο, Πυρίτιο, Ημιαγωγοί, Τρανζίστορ, Νόθευση n-τύπου, Νόθευση p-τύπου, Διάχυση φορέων, Νόμος του Moore, Ge MOSFET, Ανίχνευση υπέρυθρων ακτινοβολιών

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Abbreviations

BI	Boron Interstitial
BJT	Bipolar Junction Transistor
CMOS	Complementary Metal Oxide Semiconductor
Ge	Germanium
HPGe	High Purity Germanium
IR	Infrared
JFET	Junction Field Effect Transistor
MOSFET	Metal Oxide Semiconductor Field Effect Transistor
NMOS	N-channel Metal Oxide Semiconductor
PMOS	P-channel Metal Oxide Semiconductor
SET	Single Electron Transistor
Si	Silicon

Chapter 1

Introduction

Materials have always been an integral part of the science of electrical engineering, from the need for good insulators capable of handling hundreds of volts to the need for good conductors capable of handling hundreds of amperes. The dielectric properties of materials are fundamental in the design of capacitors or permanent magnets. The creation of high-purity single-crystal conductors has always been a crucial point for the development of the semiconductor industry. Materials continue being a fundamental part of the science of electrical engineering up to nowadays. The creation of single-crystal silicon wafers with a diameter of 12 inches, and on the opposite scale, the creation of layers of different semiconductor materials with thicknesses in the range of tens of angstroms, are fields of ongoing research. The properties of high-purity single-crystal materials are fundamental for designing a large number of semiconductor devices. The reason why scientists and engineers put their notice on materials is that their properties and characteristics define the quality of life of people. Materials play a significant role in enhancing the quality of life for several reasons. Materials enable the development of advanced technologies, such as smartphones, computers, and medical devices, which facilitate communication, information access, and healthcare. It also obvious that materials with specific properties contribute to the creation of efficient and sustainable energy systems, including renewable energy sources and energy storage solutions. They enable the construction of safe and durable infrastructure, from buildings to transportation networks. Healthcare is another domain in which they play a significant role such as the manufacturing of biocompatible implants and drug delivery systems to improve medical treatments and enhance the well-being of individuals. So it is clear that materials innovation drives progress and positively impacts various aspects of people's lives.

1.1 Materials categorization based on their conductivity

Materials can be categorized into different conductivity classes based on their ability to conduct electric current. Conductivity refers to the ability of a material to allow the flow of electric charge. Below we describe the three main categories of materials:

1.1.1 Insulators

Insulators are materials of low conductivity that do not easily allow the flow of electric charge through them. Their low conductivity is due to their unique atomic or molecular structure, which inhibits the movement of charged particles, such as electrons. Their low conductivity, means that they do not conduct electricity effectively. So, when an electric field is applied to an insulator, the charged particles within the material do not move freely. Instead, they are tightly bound within the atoms or molecules of the insulator, and do not have the mobility to flow and carry an electric current. The lack of conductivity in insulators makes them useful in a variety of applications. Insulators are commonly used as electrical insulation materials to prevent the flow of electricity where it is not desired, such as in wires and cables. Insulators are also utilized in electronic devices and systems to prevent short-circuits and ensure proper electrical isolation between different components or circuits. Insulating materials include rubber, plastic, glass, ceramic, and wood. The conductivity of insulators can be affected by various factors, such as temperature, pressure, and moisture.

1.1.2 Conductors

As opposed to insulators, conductors are materials of high electrical conductivity. This means that they allow the flow of electric current through them. Examples of conductors include metals, graphene and carbon materials. Conductors conduct the electric charge typically in the form of electrons. They are characterized by high electron mobility which means that they have a high concentration of free electrons, low energy barrier for their electrons to move between energy bands and high thermal conductivity. We have to mention that they play a crucial role in various fields such as energy transmission, communications and electronics.

1.1.3 Semiconductors

Semiconductors is a class of materials that exhibit intermediate conductivity between conductors and insulators. The electrical conductivity of semiconductors can be controlled and modified through various methods, such as doping, temperature, and applied electric fields. There are elemental semiconductors that are found in the IV group of the periodic table and compound semiconductors that are formed by the combinations III-V, II-VI, IV-IV of the elements of the respective groups of the periodic table. Apart from the binary alloys of semiconductors there are also ternary and tetrahedral alloys.

1.2 Germanium

Germanium is a chemical element which is located on the periodic table of elements in Group 14 or IVa and period 4. Its position is between Silicon (Si) and Tin (Sn). We can clearly see its position on the periodic table of elements in Figure 1.1, where the periodic table is displayed with the element Ge being marked out. The symbol used to refer to it is Ge. In the subsections below we are going to analyse briefly some of the basic characteristics of Germanium:

The periodic table displays elements from 1 to 118. Germanium (Ge) is located in Group 14, Period 4, with atomic number 32. It is highlighted in blue. The table includes the Lanthanide Series (elements 57-71) and the Actinide Series (elements 89-103) at the bottom.

1	2											13	14	15	16	17	18
1 H Hydrogen 1.008	2 He Helium 4.003											13 B Boron 10.811	14 C Carbon 12.011	15 N Nitrogen 14.007	16 O Oxygen 15.999	17 F Fluorine 18.998	18 Ne Neon 20.180
3 Li Lithium 6.941	4 Be Beryllium 9.012											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.948
11 Na Sodium 22.990	12 Mg Magnesium 24.305	3	4	5	6	7	8	9	10	11	12	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 52.00	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.69	29 Cu Copper 63.546	30 Zn Zinc 65.38	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.757	52 Te Tellurium 127.6	53 I Iodine 126.905	54 Xe Xenon 131.29
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 98.906	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.905	46 Pd Palladium 106.37	47 Ag Silver 107.868	48 Cd Cadmium 112.415	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium 209	85 At Astatine 210	86 Rn Radon 222
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71 * Lanthanide Series	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.084	79 Au Gold 196.967	80 Hg Mercury 200.59	113 Nh Nihonium 284	114 Fl Flerovium 289	115 Mc Moscovium 288	116 Lv Livermorium 293	117 Ts Tennessine 289	118 Og Oganesson 294
87 Fr Francium 223	88 Ra Radium 226	89-103 ** Actinide Series	104 Rf Rutherfordium 261	105 Db Dubnium 262	106 Sg Seaborgium 266	107 Bh Bohrium 264	108 Hs Hassium 277	109 Mt Meitnerium 268	110 Ds Darmstadtium 271	111 Rg Roentgenium 272	112 Cn Copernicium 285	113 Nh Nihonium 284	114 Fl Flerovium 289	115 Mc Moscovium 288	116 Lv Livermorium 293	117 Ts Tennessine 289	118 Og Oganesson 294

ChemistryLearner.com

Figure 1.1: Ge location on the periodic table of elements [1].

1.2.1 Atomic number and Mass number

We distinguish the atoms of different chemical elements by the atomic number. The atomic number whose symbol is Z is defined as the number of protons which are located in the atom's nucleus and thus, the number of electrons that move around the nucleus as well. Because the atomic number defines each different chemical element it is somehow indicative of the chemical behavior of its atoms because it shows the number of electrons in them which are responsible for the chemical properties of the atom. Ge's Z is 32. The mass number whose symbol is A is the number of nucleons in an atom. Nucleons are the particles of an atom's nucleus and more specifically the neutrons and the protons. Different isotopes of the same chemical element have different mass numbers. In nature, there are five stable isotopes of Ge. The mass numbers of the five different stable isotopes of Ge are: 70, 72, 73, 74, 76. Also, Ge has radioactive isotopes, 27 in particular. Some of the mass numbers of the most common radioactive isotopes are: 65, 66, 67, 68, 69, 71, 75, 77 and 78. Their half-lives vary from 20 ms up to 287 days [2].

1.2.2 Relative Atomic mass

Atoms of different elements have different atomic masses. The atomic mass is the amount of matter in each atom. Even though someone would expect that we can find the atomic mass if we summarize the masses of electrons, protons and neutrons of each different atom this is not exactly correct. In fact, the atomic mass is a little less than this summary because when these particles are combined, energy is released. Scientists focused on finding a way to calculate the masses of the atoms immediately after Dalton's atomic theory was established. Since the size of the atoms is inconceivably small it was difficult to directly calculate their masses. So, the masses of each atom are calculated using a specific mass unit, the atomic mass unit briefly amu. The amu is defined as the $1/12$ of the mass of the atom of Carbon (C) with mass number 12. If we want to express the amu in the SI we have to mention that 1 amu is equal to $1.66053907 \times 10^{-27}$ kilograms. The relative atomic mass which can also be referred to as atomic weight of an atom is a number that shows us how many times is the atom's mass bigger than that of the $1/12$ of mass of the atom of C with mass number 12. For Ge the atomic weight is equal to 72.630u.

1.2.3 Additional important chemical and physical properties of Ge

Ge's electron configuration is $[Ar]3d^{10}4s^24p^2$ and its atomic radius which defines the size of each atom is $1.52\text{\AA}$. It has 4 valence electrons which means that there are 4 electrons in its outer shell. This information is extremely important especially when we are going to analyze the doping behavior of Ge in Chapter 2. Its density is 5.3234 gcm^{-3} . Also, we have to mention that it is metalloid which means that it has properties of both metals and non metals. Metals are the chemical elements that expose high thermal as well as electrical conductivity. On the opposite non metals are generally of low electrical conductivity. At room temperature in particular 20 degrees Celsius it is solid. Its melting point (point at which it turns liquid) is 937.4°C and its boiling point (point at which it turns gas) is $2,830^\circ\text{C}$. Its colour is Greyish white and it is lustrous and brittle [3]. In Figure 1.2 we can see a chunk of ultrapure polycrystalline (composed of many small crystals) Ge weighing 12 grams

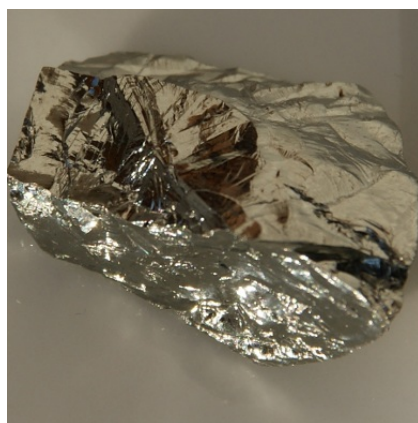


Figure 1.2: Ge is lustrous, Greyish white and brittle [4].

1.2.4 Abundance

Ge's abundance on the crust of the Earth is calculated as 1.5 parts per million and 0.42 parts per million by weight and by moles respectively. As far as the solar system it concerned, its abundance is 200 parts per billion and 3 parts per billion by weight and moles respectively. Its abundance is higher than that of the elements Cd, Hg, As and Cd but lower (on the earth's crust) than many elements which are heavier than it like Ba, Br, Sr, Hg, Sn etc. If we want to compare its abundance with that of Si we understand that the difference is chaotic. Si composes the earth's crust at a percentage of 27.7%. It is worth noting that it is the second most abundant natural existing chemical element on earth. The first one is O. In the solar

system its abundance comes after H, O, He, C, Ne, N. That is why Si is a kind of constant to compare the abundance of different elements. Instead of just calculating the direct value of the element's quantity per million parts, scientists compare it to the amount of Si. The comparison is per 1 million atoms of Si, in simpler words how many atoms of element exist per 1 million atoms of Si. For, Ge this value is 50.5.

1.2.5 Use in medicine and consequences to people

Apart from its use as a semiconductor which we are going to extensively discuss in this thesis Ge is in some cases used in medicine to cure cancer and other diseases. But, elemental Ge is reported to be unsafe in some cases. Its compound with Oxygen Germanium oxide is dangerous for human health when consumed. There are more than 30 reports of severe cases like kidney failure and death have been associated with consuming Ge. It is possible to damage vital organs such as the kidney because it builds up in these organs.. Other consequences include anemia, muscle weakness, nerve problems, etc [5].

1.3 Transistor

Since the building block of nowadays ICs which compose our electronic devices is the transistor we see fit to briefly describe it at this point. So, it is made out of semiconductor material which goes through many stages of processing and its purpose is to amplify or switch electrical signals and power. It is fabricated out of semiconductor material (amongst which Ge), and it has three terminals for connection to the IC. When a voltage or current is applied to one pair of the transistor's terminals the current through another pair of terminals is controlled. There are two main categories of the which we are going to analyse in chapter 3: Bipolar Junction Transistors (BJTs) and Field Effect Transistors (FETs).

1.4 Thesis goals

In this thesis we are going to focus on semiconductor materials and, in particular those who consist of the chemical element Ge. Ge is used in various microelectronic applications even though Si is the chemical element which is now dominating semiconductors' industry. We are going figure out why Ge has been overshadowed by Si in microchips fabrication and

what are the possibilities of it being used in more applications. This will be succeeded by analysing its properties, the characteristics of computers' electronic components, the history of Ge in semiconductors' industry starting from the first transistor which was made of it and in the end the comparison of Ge's and Si's properties.

Chapter 2

Germanium properties and technology

2.1 Doping

If we want to give a brief definition of doping, that would be that it is a process that takes place in order to change the number of holes or electrons (depending on the type of the doping) in a semiconductor. When an intrinsic semiconductor (a semiconductor with no impurities in its crystal) is doped then it becomes extrinsic (a semiconductor with impurities in its crystal). By modifying the balance of holes and electrons in the semiconductor's crystal lattice which happens when other atoms are introduced in it, its electrical properties change depending on the type of the doping and the degree to which the semiconductor gets doped.

2.1.1 n-type doping

Semiconductors are divided into two categories depending on the chemical properties of the atoms they are doped with. There are n-type semiconductors and p-type semiconductors. To be more specific, Si and Ge have 4 outer electrons. Doping is a chemical reaction that results in the formation of ionic bonds between the atoms that introduce the impurities and the Si or Ge atoms, in their crystal. When we want to achieve n-type doping, we add for example As or P to the semiconductor crystal lattice. We have to note that the impurity element is introduced in small quantities because the purpose is to maintain the crystal integrity of the base semiconductor. These elements have five outer electrons, one more than Ge and Si have in their outer orbitals. They are known as pentavalent impurity elements. When such elements are introduced into the semiconductor crystal lattice each of their atoms forms covalent bonds with four Si or Ge neighbouring atoms. It becomes clear

that the fifth outer electron cannot form a bond and it is free to move around the crystal, so that each impurity atom donates one electron to the semiconductor. So, the number of electrons for conduction rises and the number of electrons exceeds the number of holes in an n-type semiconductor. This presence of pentavalent impurities introduces loosely bonded electrons into the lattice structure. We can visualise an n-type semiconductor on the left hand side of Figure 2.1. When we apply a certain voltage these electrons gain enough energy to break free from their bonds and move across the forbidden energy gap and they transit from the valence band to the conduction band. So, only a small number of holes remain in the valence band. Due to the flow of electrons into the conduction band, the Fermi level, which represents the highest energy level occupied by electrons at absolute zero temperature, is positioned close to the conduction band.

2.1.2 **p-type doping**

When we want to form a p-type semiconductor we introduce elements such as B or Ga into the semiconductor crystal lattice. These elements have 3 three electrons in their outer orbitals, one less than Si or Ge (as opposed to the elements we use to achieve n-type doping). So the outer electrons of the atoms of the semiconductor are inadequate to form covalent bonds with all of the outer electrons of the impurity element's atoms. At one position there is no bond so holes are formed which are the majority carriers of p-type semiconductors and lack one electron each. The holes that are formed in the valence band of the atoms of Ge or Si make the electrons in this bagermaniumnd mobile. This results in the holes movement in the opposite direction to which the electrons move. The only charges that can move into the lattice are the positive ones. In Figure 2.1 on the right hand side a p-type semiconductor is demonstrated. When we have doped semiconductors materials there is more of one type of carrier than the other, meaning that we have more holes than 'free' electrons or vice versa. The carrier with the biggest concentration is the majority carrier and the other is the minority carrier.

N-type and p-type doping mechanisms are applied in order to change the electrical properties of the material they are introduced into. Their most integral differences are aggregately being mentioned in Table 2.1.

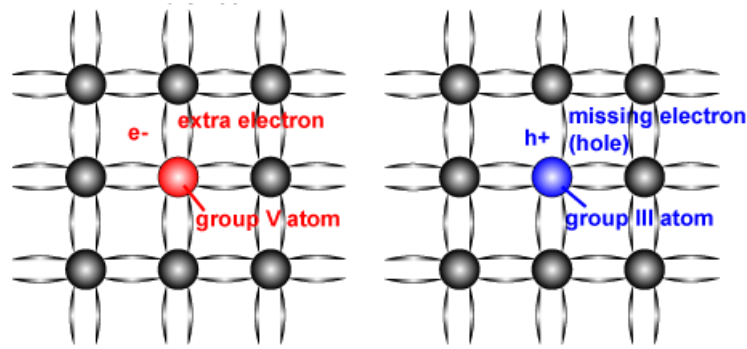


Figure 2.1: n-type semiconductor(left) and p-type semiconductor(right) [6].

Table 2.1: Main differences between p-type and n-type doping [6] [7] [8].

	n-type	p-type
Group of impurity element (periodic table)	V	III
Number impurity element's outer electrons	5	3
Bonds	Excess electrons	Missing electrons
Majority carrier	Electrons	Holes
Minority carrier	Holes	Electrons
Majority carriers movement	Lower to higher potential	Higher to lower potential
Impurity elements' characterization	Donor atoms	Acceptor atoms
Impurity element's energy level	Close to the conduction band	Close to the valence band

2.1.3 Ge doping

The process of doping Ge with high concentration impurities has many confrontations because it is difficult to activate impurity atoms to the required degree. It is also hard to prevent their escape when thermal treatments take place and also to not disturb the semiconductor's crystal integrity. We can say that the most demanding aspect of impurity doping in n-type

Ge devices has to do with the source and drain regions. P and As impurities are difficult to activate and have the tendency to diffuse rapidly. This means that there is no big potential to limit the device's dimensions and there are high access resistances. Sb is a heavy ion and as a result it can possibly cause severe substrate deformation when ion implantation is performed. On the opposite, p-type trivalent dopants with the most commonly used being B and Ga, are of relatively low diffusivity and in addition to their high electrical activation in Ge, they are the perfect elements for scaled junction formation [9].

2.2 Diffusion

2.2.1 Acceptor diffusion in Ge under thermal equilibrium

Under thermal equilibrium circumstances, vacancies are the ones that dominate in Ge and that can be easily understood by studying the diffusion behavior of B. The relatively slow diffusion of B can be noted by its diffusion coefficients which are less than Ge self diffusion rates. This property is opposite to the one of Si, where foreign atoms' diffusion is being in general faster than that of self-atoms since the activation diffusion enthalpy of self diffusion is higher than that of the foreign atoms, indicating a sufficient binding energy amongst the foreign atom and vacancies or interstitials [10]. In Ge the obvious lack of interstitials which is due to its high formation enthalpy obstructs foreign atoms to be diffused that preferentially bind with interstitials instead of vacancies. Abstract measurements prognosticate a revolting interaction between vacancies and B and this is due to lattice strain from the small size of B and its closeness to the next nearest vacancy [11]. Interstitials are the ones that help reduce the strain around isolated substitutional B by the promotion of B diffusion through the formation of Boron interstitial (BI) pairs. But we have to point out that because of B diffusing slowly under thermal equilibrium, the total amount of interstitials and BI pairs is inadequate to result in mass transport in Ge.

If we want to make a comparison with p-type dopants, we could take In as an example. In's atomic radius is larger than that of Ge. This leads to Ge's crystal lattice being expanded significantly when embodied into the substitutional site. Theoretical calculations indicate an attractive interaction between In and vacancies on the first and second nearest neighbor sites, but a repulsive interaction on the third nearest neighbor site. As for In's diffusion vacancy ring mechanism, the vacancy needs to transport to at the minimum the third nearest neighbor

position in order to perform a complete diffusion jump. It is also important for the vacancy to approach In from another side. This repulsive interaction affects the overall activation enthalpy of In diffusion, which is experimentally observed to exceed the activation enthalpy of self-diffusion, with In diffusion magnitude being similar to or in worst case slightly higher than Ge self-diffusion. These findings support the complex interaction between In and vacancy which have been documented by various theoretical calculations. Some further insights into the point defects involved in In diffusion in Ge are obtained from its behavior under intrinsic and extrinsic doping conditions. Experiments demonstrate that the InV pair is has negative charge as it happens with substitutional In which means that In diffusion is not proportionate with p-type doping levels. Similar diffusion behavior has been observed for Ga in Ge [12].

2.2.2 Donor diffusion in Ge under thermal equilibrium

When we talk about donor diffusion in Ge, we have to consider the n-type dopants. As we have already mentioned such dopants are the elements like P, As and Sb. By studying the intrinsic as well as the extrinsic diffusion behavior of such dopants in Ge, it has been observed that the diffusion is more effective when extrinsic doping is performed. When the concentration of the intrinsic carrier is higher than the concentration of the dopant then intrinsic diffusion is possible. The temperature at which the diffusion takes place plays a significant role. On the opposite, the extrinsic diffusion mechanism takes place when the intrinsic carrier concentration is lower than that of the dopant. Inside the crystal an electric field is created which results in a force put on the dopant atoms which are diffused. In order to precisely model the dopant diffusion we have to consider the vacancy mechanism and note vacancies which are double negatively charged and the dopant vacancy pairs which are singly negatively charged. The experimental studies have focused on donor diffusion is because the n-type dopants we mentioned before diffuse significantly quicker in Ge than B and other p-type dopants [13] [14]. Even though in Si crystals in the n-type dopants diffusion both vacancies and interstitials play a significant role, in Ge only the understanding of the vacancies behavior is enough to describe the diffusion mechanism [15]. In Figure 2.2 we can see some measurements conducted with spreading resistance profiler after the intrinsic and extrinsic diffusion of As in Ge. The curve which represents an As(dopant) concentration of 10^{17} cm^{-3} refers to the intrinsic diffusion and the curve that represents an As(dopant) concentration of

$6 * 10^{19} \text{cm}^{-3}$ refers to the extrinsic diffusion. The diffusion took place at a temperature of 820 degrees Celsius and the measurements were taken after 6000s after the diffusion mechanism started. From the curves it becomes clear that As has better diffusion properties when extrinsic diffusion is performed [16]. As intrinsic diffusion the enthalpy needed to activate the diffusion mechanism is inversely proportional with the size of the dopant. This is because of the binding energy amongst the doping element and the vacancy. When extrinsic diffusion is performed the dopant diffusion coefficient is analogous to the square of the concentration of the free electrons.

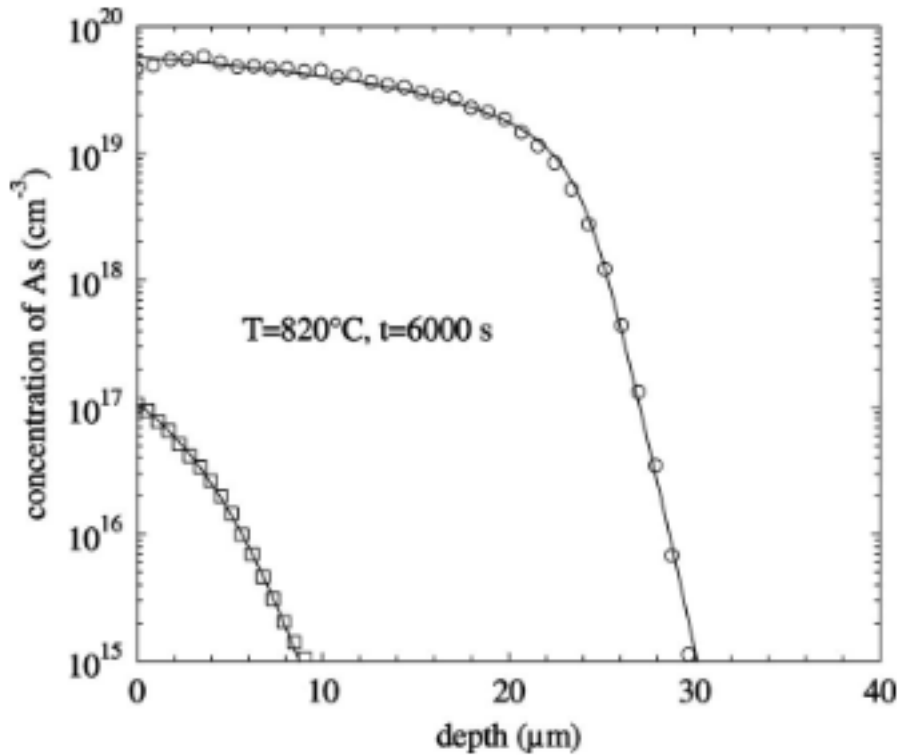


Figure 2.2: Dopant concentration profile after intrinsic and extrinsic diffusion of As in Ge at certain temperature and after certain period of time [16].

Chapter 3

The evolution of the transistor and the switch to Si from Ge

3.1 Introduction

In this section we are going to analyze how the first transistor was made, what were the early year optimisations after it was discovered and the reasons why the semiconductor industry switched to Si for manufacturing transistors even though the first ones were made out of Ge. We are going to refer briefly to the categories of transistors we have today and the give the reasons why Si has dominated transistor manufacturing up to day.

3.2 Transistor technology evolution

In 1947 the first transistor was invented at Bell Labs. Even though during the first 7 years Ge was used to manufacture transistors, in 1954 they switched to Si.

3.2.1 The invention in 1947

The invention of the first transistor -which we can see in Figure 3.1- was a significant breakthrough in the field of electronics since it changed the world forever. The whole venture was a result of the tireless research attempts and and effective cooperation by a team of scientists and engineers at Bell Labs. The journey that resulted in the development of the first ever transistor began in the late 1940s when scientists at Bell Labs set the goal to replace fragile and power-hungry vacuum tubes that were commonly used for electronics until then

with a more efficient gadget [17]. Three unknown scientists (up to then) were those that were involved in the process that was meant to end up in the creation of the state-of-the-art invention of the 21st century. It would be a big omission if we did not mention their names. They were John Bardeen, Walter Brattain, and William Shockley. It was them that were the first to recognize the potential of semiconductors and in particular Ge, bringing a revolution to electronics. Since they had decided to put their focus on Ge they tried to analyze the properties of this chemical element which was a crystalline element with unique conductivity characteristics. In 1947, it was Bardeen and Brattain that made the crucial breakthrough and laid the foundation for the technology we enjoy today. They managed to discover the point-contact transistor, which was made out of a small piece of Ge with point contacts made of gold. In order to gain a better understanding of its structure and layers, we can see its schematic diagram in Figure 3.2. The transistor was able to amplify electrical signals effectively by applying voltage to these point contacts. This was the first transistor discovery and even though it was far from perfect due to its dimensions it was the start for the future advancements that followed in transistor technology. Shockley was the one who played the most significant role in the invention of the junction transistor by building on the work of Bardeen and Brattain. Two years after the invention of the first transistor, in 1949, Shockley designed a pattern that incorporated multiple layers of Ge with carefully controlled doping. This structure made it more effective in controlling the current flow, giving the transistor enhanced properties [18]. The technological revolution in electronics had already started but there was a long way to go yet till the transistors could be utilized the way it is today.



Figure 3.1: Picture of the first transistor [19].

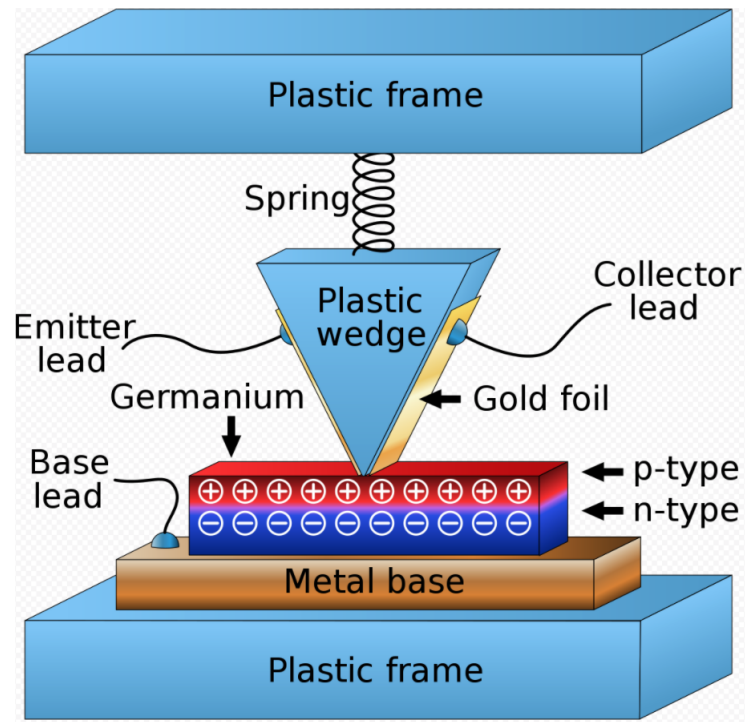


Figure 3.2: Schematic diagram of the first transistor [20].

3.2.2 The scientific phase

Even though within a short period of time the point contact as well as the junction transistor had been invented they were not ready yet to get into mass production. In 1948, G.K. Teal and J.B. Little grew a single crystal of Ge, which made possible the detection and characterization of minority carriers. After many experiments conducted by Haynes, Pearson, Suhl, and Shockley, they were able to understand the behavior of minority carriers and they were provided with measurements on various parameters. These experiments showed that Shockley's junction transistor theory could be applied to create practical devices. But yet, the crystal growth techniques had to be improved as well as techniques for controlled doping. In 1950, Shockley, M. Sparks, and Teal successfully grew a crystal with a thin p-type region embedded in n-type material, leading to the fabrication of n-p-n rods and the application of contacts [21]. The electrical properties of these devices proved the theory that Shockley had expressed. In 1950 Shockley published his book with the title "Electrons and Holes in Semiconductors," which played a crucial role in gaining knowledge and understanding of semiconductors and transistors. After five years of hard work the invention of the transistor became complete and understood by the scientists. The engineering phase was now ready to start.

3.2.3 Czochralski method development

Successful scientists' interest was rapidly attracted to this new invention. As more information emerged about it more and more scientists gathered at Murray Hill to gain information and join the transistor group. Simultaneously, activities related to the transistor were taking place in other sections of the laboratory. One notable achievement was made by Gordon Teal, who successfully adapted the Czochralski method to grow single crystals of Ge from a molten source. These crystals, became popular for their near-perfection and enhanced purity and thus, quickly gained popularity within the transistor project. We can see the mechanism of the method in Figure 3.3. After the growth of these crystals, Shockley developed an elegant theory concerning the electronic properties of the pn junction in Ge and Si. His contribution to the development of the pn junction theory opened the way for a more efficient transistor structure, that consisted of two closely spaced junctions with alternating conductivity types (npn) embedded within the crystal itself. According to Shockley's theory, the transistor action would take place entirely within the crystal's interior. The author put his focus on investigating Ge pn junctions, primarily obtained from cast ingots. Although these junctions occasionally formed during solidification, their characteristics varied from sample to sample, and their agreement with theory was not what is was supposed to be. In order to overcome these problems, the author and their team constructed a crystal growth apparatus based on G.K. Teal's work. This equipment allowed for the controlled addition of donors or acceptors during crystal growth, which resulted in making easier the formation of pn junctions within the continuous crystal. The junctions that we formed exhibited rectification properties that conformed remarkably well with Shockley's theory. This achievement gave the team the motivation to pursue the development of the junction transistor. The successful operation of the junction transistor relied on injecting minority carriers across a forward-biased pn junction. With further refinements in the controls, they were able to produce crystals with a small npn section, which was the the essential component of a functional transistor and confirmed the predicted operating characteristics [21]. While the technique of growing junctions in crystals was eventually surpassed in practical transistor manufacturing, its significance is not doubted. This approach provided useful information into the basic physics of transistor action. We have to mention that the successful growth of pure crystals with adequate minority carrier properties was a matter of luck to a certain degree. We could not leave unmentioned that the very first crystal grown possessed a minority lifetime of 100 seconds, surpassing the

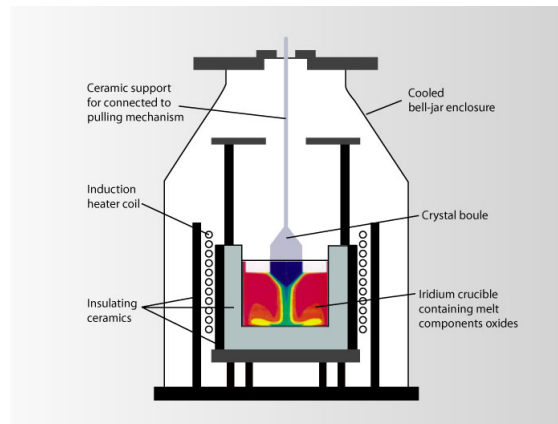


Figure 3.3: Czochralski method explained [22].

requirements for high-frequency operation above 10 megacycles. The development of the Czochralski method benefited the technical community and society as a whole since crystals with such properties of purity etc could not be found in nature.

3.2.4 Enigneering phase

Even though many optimizations were made even from the initial stages of the development of the transistor engineers found it difficult to put in large scale manufacturing. That happened because the available transistor structures were not suitable for such an action. The point-contact transistor, with its roots in cat's whisker technology, had limitations that prevented it from being manufactured in large scale. It was a complex and difficult device to fabricate, resulting in variable electrical characteristics that were hard to control and were unstable. But these limitations did not prevent, Western Electric, a division of AT&T, from manufacturing point-contact transistors for nearly a decade. These transistors were used in telephone oscillators, hearing aids, automatic telephone routing systems, and even the first airborne digital computer. Manufacturing engineers and circuit designers were not satisfied about this type of transistor due to its limitations. It was the junction transistor that exhibited more predictable and desirable electrical properties. There were challenges in terms of material usage and required complex techniques for establishing contacts. The process involved growing crystals with precise doping procedures in order to create a thin layer of base material nestled between opposite-type emitter and collector materials. Each crystal could give only a single slice of base material, which was then cut into rods. These rods contained the base material, and very careful efforts were made to locate and establish contacts with the

base layer in each rod. The difficulties of this process limited the possibilities of automation. Despite these obstacles in 1952, progress was made and the grown junction transistor entered the manufacturing stage. During this period J. E. Saby of General Electric introduced the alloy junction transistor. This innovative transistor design involved the alloying of In dots, acting as an acceptor material, on both sides of thin slices of n-type Ge [23]. The manufacturing process started with the growth crystals with uniform doping, which proved to be more manageable. The slices that these crystals gave were positioned in jigs, where arrays of In dots were strategically placed. After the alloying process, the slices were diced, resulting in a large number of individual transistors. Applying contacts to these transistors was an easier task. The alloy transistor exhibited stable and consistent performance characteristics, effectively taking the most out of semiconductor material, and enabling some degree of batch processing and automation. It became the first commercially viable transistor and remained a the most significant part of the industry for several years. But, achieving the required thin base layers for optimal high-frequency performance needed precise control over dimensions and alloying temperatures.

The development of the alloy junction process also had an unexpected outcome since it facilitated the fabrication of a functional field-effect transistor. Shockley had considered again the field-effect transistor in 1951, this time as a junction device. His concept involved using the space-charge region of a reverse-biased junction to restrict the flow of majority carriers in a semiconductor material. According to his analysis, this configuration could generate power gain. Since the device relied only on majority carriers, it was referred to as a unipolar transistor, distinguishing it from the bipolar junction transistor that involved both minority and majority carriers. In 1952, Shockley encouraged G. C. Dacey and the author to engage with the project of constructing a unipolar field-effect transistor. To simplify the structure, they opted for alloying indium over the surfaces of an n-type filament to create the gate region, process that was based on Shockley's theoretical framework [23]. Although this approach gave the expected behavior, it did not offer significant performance advantages over the bipolar transistor and there were comparable challenges during fabrication. Inevitably, while the field-effect theory received validation, the field-effect transistor was not massively manufactured for the time being.

3.2.5 Switch to Si

Si put it's toll as the preferred material for transistor manufacturing due to several forceful reasons. That happened because it was evident that Si possessed significant advantages over Ge for most applications. One of the most important reasons contributing to this preference was the higher energy gap of Si, measuring 1.1 eV compared to Ge's 0.67 eV [24]. This main difference meant that in Ge, even at room temperature, a big number of electrons could overcome the energy gap and enter the conduction band. Due to that, the reverse current in Ge pn junctions was beyond the limitations and increased rapidly with rising temperature. This did not happen with Si because it exhibited orders of magnitude smaller reverse currents and it made reverse-biased Si junctions behave more like open circuits. This characteristic made Si much more suitable for relay-type operations commonly found in logic and switching applications. The Si junctions maintained their properties even at significantly higher temperatures compared to Ge. This made them understand that Si had a higher capacity to handle power and retain its functionality in demanding environments. The reverse current in Si was significantly lower, making it more suitable for practical applications.

But apart from the advantages, there were a few minor disadvantages that were associated with Si. There was a higher energy gap which meant that a higher forward bias voltage was required to start a significant flow of current. So it becomes clear that Si circuits operated at higher minimum voltages, which required increased power consumption. Si also exhibited lower minority carrier mobility and that resulted in reduced carrier velocity and posed a lower limit on operational speed but advancements in miniaturization technology helped mitigate this limitation by allowing for smaller device dimensions. The main reason why using Si was hard was the requirement for crucial chemical and metallurgical processes to be carried out at comparatively higher temperatures compared to Ge. Si had a melting point of 1415°C as opposed to 937°C for Ge. Si was more chemically reactive than Ge. These higher processing temperatures and reactivity made it difficult in terms of achieving the required material purity and crystal perfection. The materials used to contain Ge during crystal growth either failed under Si growth temperatures or had high levels of contamination [21]. To overcome these obstacles, huge efforts were made to develop Si transistor capabilities. Researchers successfully produced Si crystals by pulling from a melt contained in a Si crucible. The problem was that the resulting crystals were heavily contaminated with oxygen from the Si. The issue of contamination was successfully managed through the development of the floating zone

method, which allowed for the creation of a zone of molten Si material contained only by surface tension. By moving the Si rod relative to the heating element, the molten zone could now be traversed within the crystal, enabling the application of zone refining techniques to achieve high crystal purity that could be compared to this of Ge.

3.2.6 Si domination

Seven year after the initial invention of the transistor, in 1954, the first Si transistor that could be massively manufactured was created by using the grown junction method. This progress made Si devices popular among the semiconductors' industry. What they could assume was that Si would dominate logic and switching applications and Ge would continue to be used in high-frequency linear applications [24]. Si technology evolved so rapidly that Si dominated the semiconductors industry over Ge.

3.3 Categories of transistors

There are two major categories of transistors Bipolar Junction Transistors (BJTs) and Field Effect Transistors (FETs). We are going to discuss FETs more analytically.

3.3.1 Bipolar Junction Transistors (BJTs)

BJTs are transistors that have three divisions of semiconductors, either n-p-n (NPN transistors) or p-n-p (PNP transistors). They contain three terminals: the emitter, the base, and the collector, which are connected to the respective divisions of the semiconductor. In a PNP BJT, the base terminal is connected to the n-type semiconductor, while the emitter and collector terminals are connected to the two p-type semiconductors as shown in Figure 3.4. In an NPN BJT, the base terminal is connected to the p-type semiconductor and the emitter and collector terminals are connected to the two n-type semiconductors as shown in Figure 3.6. The BJT functions because of the flow of both electrons and holes and that is why it is considered as a bipolar device. When a small current is applied to the base terminal, it controls the flow of a larger current from the emitter to the collector. This current amplification that BJTs makes them suitable to be used as electronic switches or amplifiers. We have to point out that only when input current is applied to the base terminal BJTs become turned on. The symbols of PNP and NPN BJTs are demonstrated in Figures 3.5 and 3.7 respectively.

There are three regions of operation for BJTs:

1. Cut-off Region: In this state, the transistor is in off mode as no current flows through it. It behaves as an open switch and prevents current flow between the emitter and collector
2. Active Region: Here the BJT operates as an amplifier. The input current at the base controls the larger current flowing from the emitter to the collector and it makes possible signal amplification
3. Saturation Region: The BJT is fully on and operates as a closed switch. It allows a maximum current flow from the emitter to the collector and the transistor acts as an on-state switch

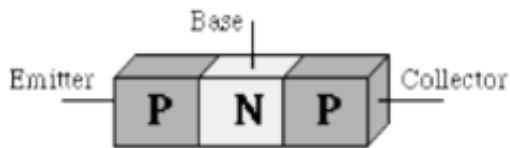


Figure 3.4: PNP BJT structure [25].

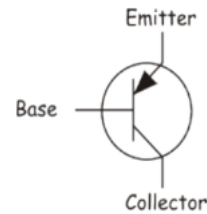


Figure 3.5: PNP BJT symbol [25].

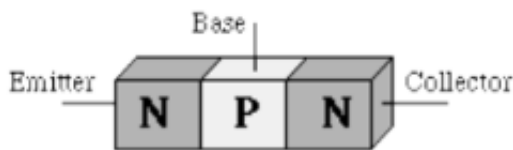


Figure 3.6: NPN BJT structure [25].

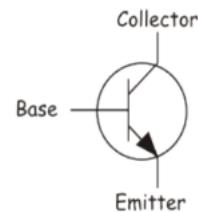


Figure 3.7: NPN BJT symbol [25].

3.3.2 Field Effect Transistors (FETs)

Another major category of transistors are the FETs. A FET consists of five parts which are the gate, the drain, the source, the insulator and the semiconductor channel. Three of these parts are the terminals of the FET transistor: the source, the gate and the drain. The FET functions by using the voltage that is applied to its gate terminal to control the current which

flows through it and this way its output current is analogous to the input voltage. The name field effect was given to them because their functionality relies on an electric field which is generated by the input gate voltage. So, it is a device operated by voltage. As we mentioned before the FET is a three terminal and unipolar device and that is why it has similar characteristics to bipolar transistors. FETs have lower power consumption than BJTs in ICs. In the previous section, we divided BJTs into two main categories: NPN and PNP. FETs are also categorised into n-channel FET and p-channel FET depending on the physical arrangement of the p-type and the n-type semiconductor materials which they are made of. The current path between the drain and the source terminals is called channel and it is either p-type or n-type. In order to control the current that flows in this channel we vary the voltage applied to the gate terminal. The FET relies only on the conduction of holes if it is p-channel or electrons if it is n-channel. FETs input impedance is comparatively high to that of BJTs. That means that they are sensitive to input voltage signals which has the disadvantage of them being easily damaged by static electricity.

Junction Field Effect Transistors (JFETs)

The Junction Field Effect Transistor (JFET) is one of the major categories of FETs. It is a three-terminal device controlled by voltage and it is used mostly in digital circuits. The unipolar field effect transistor has two pn junctions inside its structure. JFET works on the principle of depletion region and current flow is enabled through reverse biasing of gate-to-source terminals. JFET transistors are further categorised depending on the dopants: n-channel JFET and p-channel JFET. An n-channel JFET has an n-type material between the drain and source terminals. Two p-type materials are then nested along the metal contacts of the gate terminal. The usage of two p-type materials results in the formation of two pn junctions inside the JFET transistor. We also have the p-channel JFET which is composed of a p-type material between the drain and source terminals. Also, n-type materials are fixed along the metal contacts of the gate terminal. Here we have two n-type materials which correspond to the n-channel form two pn junctions. The symbols of n-channel and p-channel JFET are demonstrated in Figures 3.8 and 3.9 respectively.

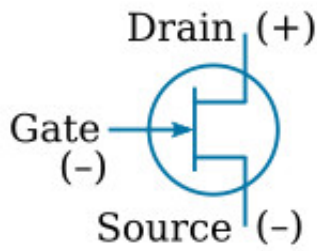


Figure 3.8: N-channel JFET symbol [26].

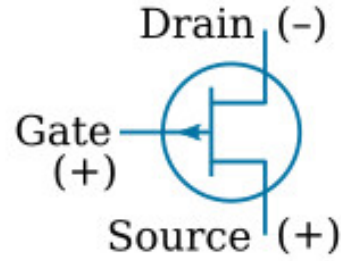


Figure 3.9: P-channel JFET symbol [26].

Metal Oxide Semiconductor Field Effect Transistors (MOSFETs)

MOSFETs are FETs with MOS structure. MOSFETs are devices of high speed and low loss operation. We can say that they are advanced FETs. An oxide layer is placed on the substrate to which the gate terminal is connected. This oxide layer acts as an insulator. When making a MOSFET a lightly doped substrate is being diffused with a heavily doped region. This substrate determines whether they are p-type or n-type MOSFETs. MOSFETs are further categorised into enhancement mode whose symbols can be seen in Figure 3.10 for n-channel MOSFET and Figure 3.11 for p-channel MOSFET and depletion mode whose symbols can be seen in Figure 3.12 for n-channel MOSFET and Figure 3.13 for p-channel MOSFET.

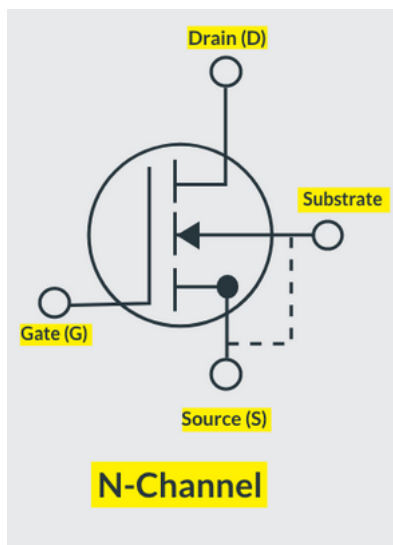


Figure 3.10: N-channel enhancement mode MOSFET symbol [27].

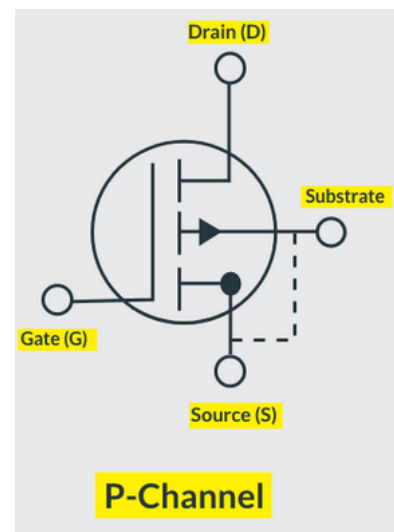


Figure 3.11: P-channel enhancement mode MOSFET symbol [27].

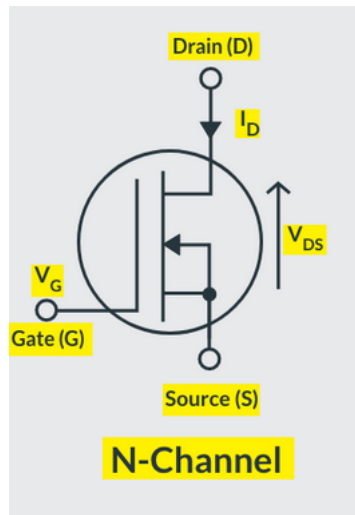


Figure 3.12: N-channel depletion mode MOS-FET symbol [27].

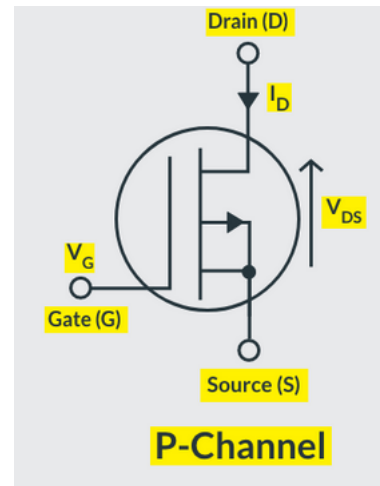


Figure 3.13: P-channel depletion mode MOS-FET symbol [27].

Chapter 4

Applications of Germanium in microelectronics

4.1 High-purity Germanium detectors (HPGe)

HPGe detectors have high efficiency in detecting photons and they have unique resolving power. These properties make them suitable for detecting X-rays as well as gamma rays and for energy spectroscopy. They are used in many fields such as sea and airborne surveillance, neutron activation analysis, in-situ environmental spectroscopy, waste assay, border security, light studies, etc. Despite their one of a kind properties related to radiation detection and satisfying energy resolution, a few drawbacks such as the inability to find adequate size material and the complexity in processing signals by the electronics, had made HPGe unsuitable for years. Since they are used in a variety of applications with different needs, there have been made optimisations relating the HPGe detector crystal growth and the detector fabrication in general. The evolution of high-speed electronics and the rising of computing power have made HPGe necessary in more applications such as biology, medicine and chemistry.

4.1.1 HPGe detectors configuration

Even though there are many kinds of HPGe detectors depending on the application they are used for we can describe their basic configuration which we can also see in Figure 4.1. The detector is a cylinder of Ge and it has a p-type contact on the surface of an axial well and an n-type contact on the outer surface of the cylinder. Ge's impurity level stands for about 10^{10} atoms/cc. This means that with moderate reverse bias, the entire volume between

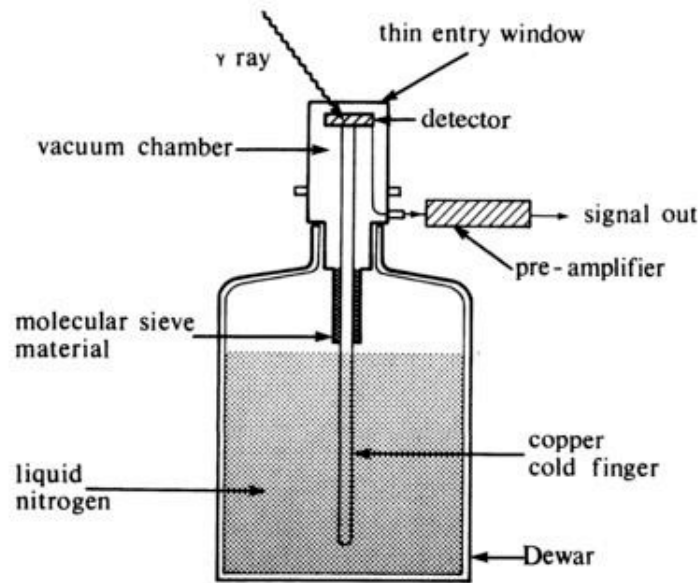


Figure 4.1: HPGe schematic diagram [28].

the electrodes becomes depleted and electric field is created all over the active region. The material used for the n contacts is diffused lithium and for the p contacts implanted boron.

4.1.2 Problems faced working with high-purity Ge

The major problem while dealing with high-purity Ge is contamination which is caused by fast diffusing impurities especially copper. In Ge at 673.15K the solubility of copper is roughly $1 \times 10^{11} \text{ atoms/cm}^3$. That means that as far as interstitial copper in Ge is concerned, at 673.15K the diffusion coefficient is about $10^{-5} \text{ cm}^2/\text{sec}$. So, if we have a 1mm thick Ge sample with 5×10^{10} donors and we heat it at 673.15K, it was going to be totally compensated by copper, given that there was copper on the surface of Ge. The amount of copper enough to get this result is just 1/1000 of a monolayer. A wafer made out of high purity Ge composes the detector and it has a p-type contact on the one side and an n-type contact on the other side. These contacts can be warmed to room temperature without being degraded and we have to mention that they are non-injecting. So, a lot of research was put during the early years of the development of HPGe detectors in order to overcome the contamination problems. A contacting procedure of low temperature (603.15K) was advanced to overcome the contamination problem which was a result of fast diffusing acceptors [29].

4.1.3 HPGe detectors' efficiency

HPGe detectors' efficiency is measured by their effective interaction volume, the degree to which it interacts with the particles it is supposed to detect. Especially, detectors used in spectroscopy had their performance improved during the last years. This was achieved by increasing the diameter of the crystal, reducing impurity levels to the minimum in order to achieve greater uniformity along the crystals' axis. The focus was put on enhancing the crystallographic properties of the HPGe crystal. Coaxial HPGe detectors have cylindrical shape with a hollow core. Their performance is analogous to their diameter which means that by increasing the diameter of the detector its performance improves. The most efficient detector up to now is a p-type coaxial detector with an efficiency of 207.6%. This detector was fabricated with specific characteristics, in particular, it has a diameter of 98 mm it is 110 mm long, its active volume is roughly 800cc and its weight is 4.4kg. Operating this detector at 3700 V, it achieves a Full Width at Half Maximum or FWHM resolution of 2.4 keV for a particle energy of 1.33 MeV.

4.1.4 Clover array

The field of nuclear reactions has been constantly evolving during the past years. Nuclear reaction studies which are being carried out involve heavy ions being bombarded onto a target. This results in the production of recoiling nuclei that decay by emitting a gamma rays. The high velocity of the moving particles causes the energy of the emitting gamma rays to be Doppler shifted and as a result the gamma ray spectra associated with the reaction becomes degraded. In order to limit the consequences of the Doppler broadening, we can minimise the acceptance solid angle of the detector. The configuration known as clover array consists of four large coaxial HPGe crystals packed closely together. The crystals are all placed inside the same cryostat in order to be cooled. The advantage of this configuration is that it allows for efficient gamma ray detection with high energy resolution. The average full width at half maximum (FWHM) energy resolution at 1.33 MeV which is a commonly studied gamma-ray energy was measured to be 1.85 keV for such a device [30]. This means that the clover array configuration can accurately measure the energy of the emitted gamma rays despite the Doppler shift caused by the recoiling nuclei.

4.1.5 30-Element XAFS array

In order to distinguish different X-ray energies with high precision, we need detectors with high energy resolution ability. X-ray absorption fine structure (XAFS) is a technique used at synchrotron radiation sources to study the local structure around atoms of interest. By analyzing the XAFS, we can get provided with information on the local structure and on the unoccupied local electronic states. In order for XAFS spectroscopy to have useful results, we need a detector that can handle a high count rate and maintain high quality energy resolution. The 30-Element XAFS array is a detector made out of HPGe. It consists of 30 individual detection channels that work in parallel. HPGe crystals are packed closely together in a circular arrangement with a diameter of 50 mm and they are all within a single detector capsule. Each channel has a 6 mm diameter and 6 mm thickness and is has a preamplifier for signal processing. This detector achieves the desired energy resolution ability. For X-rays with an energy of 5.9 keV, the average energy resolution is 147 eV at an incoming count rate of 1kcps with an amplifier time constant of 6 ms with Gaussian shaping. When the incoming count rate is 100kcps, the energy resolution is 248 eV with an amplifier time constant of 0.5 ms with Gaussian shaping [31].

4.1.6 Monolithical segmentation of the crystal

Apart from eliminating the consequences of Doppler broadening and get reliable results while performing XAFS spectroscopy, we can get additional necessary feedback from the HPGe detectors if we segment monolithically one or even both of its electrical contacts. The contacts are divided into numerous smaller elements. Each element carries signals containig the information needing to different electronics in order to be processed. In order to segment large Ge crystals into smaller elements effectively, improvements have been made in the process of photolithography as well as other methods used for crystal segmentation. These improvements in the fabrication stage of the HPGe detectors has allowed them to improve their efficiency which is measured by the effective interaction volume of the detector. With this segmentation technique, the thinner electrode of a large HPGe crystal is being separated into smaller segments and as a result it has less than 200 microns division between the different elements.

Track the Interaction of Gamma Ray Events (TIGRE)

As for n-type coaxial HPGe detectors, we can segment their thin outer electrical contact into smaller parts. The process of segmenting their contact is called photolithography. This process involves the segmentation of the HPGe crystal in two orthogonal directions. By cutting the crystal this way we get a three-dimensional closed packed volume element. This structure gives information about the position of the interaction within the Ge crystal, allowing for the reconstruction in the three dimensions or tracking of the initial path of the gamma ray. By implementing this technique, a 24-segment detector is designed and fabricated. By getting a coaxial HPGe crystal with dimensions of 6.5cm diameter and 8cm length divided monolithically into segments, we get six segments from the radial dimension and four segments longitudinally. This structure allows for better tracking of gamma ray events and provides information about their interaction positions within the crystal. The average energy resolution of the 24 segments, measured at 1.33 MeV, is 2.3 keV, indicating the precision with which the detector can measure the energy of the gamma rays. The experiments on this structure are taking place at the University of Liverpool, UK [32].

Compact Time Resolved XAFS Array INnovation (C-TRAIN)

The C-TRAIN detector -a picture of which we can see in Figure 4.2- design and fabrication was a result of the cooperation between CCLRC Daresbury Laboratory and EG&G ORTEC in 1998. The motivation for the manufacturing of the C-TRAIN came from the drawbacks multi-element solid-state detectors (MESSDs) had. The MESSDs contained 13 elements with an active area covering about 36% of the solid angle subtended by the detector to the sample. It becomes clear that when multiple diodes were packed together a large dead space was left. They understood that in order to get maximum count rate, the detector had to be placed closer to the sample and at the same time to not get in the way of the rest of the equipment. To achieve this, a very concrete detector system was necessary. Another issue was to eliminate the amount of dead space between the elements. Since, the monolithic detector was not suitable because of charge sharing between the elements they had to find another solution. So, they fabricated the C-TRAIN detector. The C-TRAIN detector features a monolithic nine-channel array with a 21.8 mm active diameter and an active area exceeding 90%. The active depth of the Ge wafer used is 6mm. The monolithic array is housed within a cryostat snout measuring 305 mm in length and 45 mm in diameter. The active surfaces of the

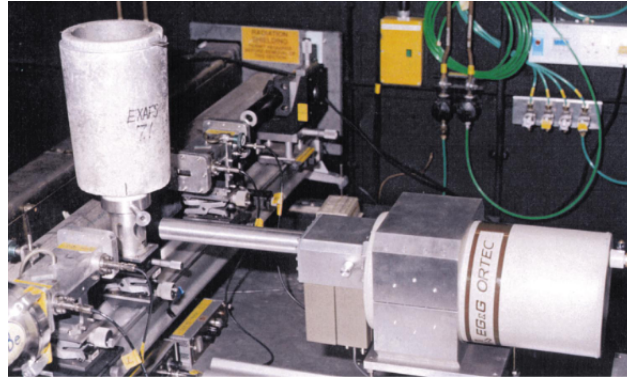


Figure 4.2: C-TRAIN detector assembly [33].

detector are positioned approximately 7 mm behind the front Beryllium (Be) window. The Be window, which is 250 mm thick, allows for an energy range above 3 keV. The concrete design of the dewar provides a holding time of over four days before it needs to be refilled. The system achieves energy resolution of 170eV when the X-ray energy is 5.9eV. The count rate per channel well is 100kcps. The system used standard analog shaping amplifiers and the semi-Gaussian shaping time is 0.5ms. These measurements indicate the detector's ability to accurately measure the energy of detected X-rays. The system with its 6mm deep Ge crystal has a satisfying output when the well is above 100keV. The serviceable energy range is 3keV and above because of the Be window [33].

4.2 Infrared imaging

Infrared (IR) imaging refers to the act of capturing and visualising Infrared Radiation (IR) (Figure 4.3). To implement this technology, we use sensors that can detect IR and then transform it into a visible image. All objects in temperatures above 0K emit IR, whose intensity depends on the object's temperature. Generally, objects with higher temperatures emit IR of higher intensity. Devices, especially cameras, used for Infrared (IR) imaging work by detecting IR with specially designed sensors and then convert it into electrical signals. After that, the signals get visually represented depending on the intensity of the IR radiation captured. We have to mention that this technology has applications in a variety of fields such as biology, medicine, surveillance especially during the night and in inspection for example to find electrical malfunctions in an object.

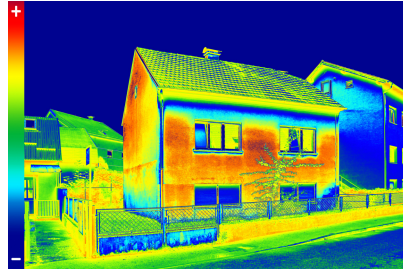


Figure 4.3: Picture taken by IR imaging camera [34].

4.2.1 Infrared Radiation (IR)

When the wavelengths of the electromagnetic radiation spectrum vary from 700nm to 1mm we have what we call Infrared Radiation (IR). In other words, IR is a segment of the electromagnetic spectrum that spans from longer wavelengths, beyond the visible red light, to the microwave range. IR cannot be seen by the human eye. It can only be felt as warmth by the human skin. We can categorize the infrared spectrum into three regions: near infrared, which is closest to the visible spectrum and has wavelengths ranging from $0.78\mu\text{m}$ to $2.5\mu\text{m}$, middle infrared, with wavelengths ranging from $2.5\mu\text{m}$ to about $50\mu\text{m}$; and far infrared, covering wavelengths from $50\mu\text{m}$ to $1,000\mu\text{m}$. When an object is moderately heated, it primarily emits infrared radiation, forming this way a continuous spectrum. We have to mention that molecules in an excited state can emit significant amounts of infrared radiation, but in a distinct spectrum consisting of lines or bands.

4.2.2 Germanium milling techniques for IR imaging applications

The knowledge around interrupted cutting of Ge was limited until the results of a survey conducted by scientists in the University of North Carolina at Charlotte, Charlotte, NC, USA, the Oklahoma State University, Stillwater, OK, USA and the Los Alamos National Laboratory, Los Alamos, NM, USA were published in 2016. Their research was focused on studying the cutting techniques for Ge so as to produce freeform optics for IR imaging applications. They conducted cutting experiments in order to gain knowledge around the subject. Their experiments involved two different cutting methods. The one was interrupted flycutting of Ge and the other uninterrupted orthogonal cutting. They took various measurements and analysed in-depth the results in order to investigate the cutting mechanisms and their impact on the surface and the subsurface of the material. The measurements were conducted using the following methods: channeling Rutherford backscattering spectrometry, atomic force mi-

croscopy and confocal Raman spectroscopy. The forces involved in these cutting processes were also measured. The reason why they put their focus on single crystal Ge was because experiments that had been conducted in the past, had come to the result that interrupted machining of single crystal Ge could result in an optical quality finish under different geometric conditions from those which were known up to then [35]. Their main goal was to understand and document the physical mechanisms that took place during interrupted machining of brittle materials especially Ge. The experiments in which orthogonal cutting was tested whose setup schema is demonstrated in Figure 4.4, resulted in the observation that as the cutting depth h decreased, the cutting force vector F_z rotated towards the normal direction of the surface of the workpiece tested. They obtained the same outcome during round-nosed flycutting method testing. They reclaimed the force coefficients which came as a result from the orthogonal cutting experiments to forecast forces in more complex flycutting scenarios. When flycutting surfaces with a feed rate greater than 3 mm/rev, atomic force microscopy (AFM) measurements indicated a highly fragmented surface with high roughness [36]. Both Raman spectroscopy and channeling Rutherford backscattering spectrometry (RBS) revealed significant lattice disorder. This outcome is consistent with low values of the cutting force coefficient, which indicates that the resultant force vector is mainly aligned with the cutting direction. As for feed rates which were less than or equal to 3 mm/rev, they did not observe significant difference in surface roughness and subsurface damage. This finding corresponds to the observed rotation of the resultant force vector towards the normal direction of the surface, which reduces the subsurface tensile stress responsible for fracture at higher cutting force coefficients. At this point, we have to mention that all of the cutting experiments that gave the results above were carried out with SCD tools with Ge workpieces which were single crystal on Moore 350 FG machine tool which was of ultra precision [37].

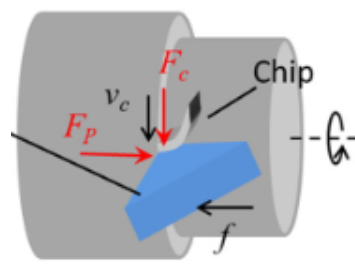


Figure 4.4: Orthogonal turning setup schema [37].

4.2.3 Infrared Fresnel lenses fabrication using single crystal Ge

As we have mentioned before Ge is used in a wide range of IR imaging applications. Single-crystal Ge is a material for infrared optics that we can consider it as irreplaceable due to its high permeability and refractive index in the 2-14 μm wavelength range. These properties make it commonly used as a substrate for infrared lenses in thermal imaging systems, optical instruments, and telescopes [38]. The demand for complex-shaped infrared optical elements, such as aspherical lenses, Fresnel lenses, and diffraction grating lenses, is constantly increasing during the last decades [39]. A Fresnel lens is a thinner version of a regular lens, achieved by cutting it into concentric rings called Fresnel zones. This design is commonly demonstrated because it reduces thickness and absorption losses. While narrower Fresnel zones are often conical, we have to mention that high-precision optical systems require spherical zones with arc cross sections. In order to have the ability to fabricate microstructures for Fresnel lenses, photolithography and diamond turning are the methods which are employed more often during the last years. If we want to explain photolithography in short we can say that it creates two-dimensional microstructures on flat substrates and this way it can achieve three-dimensional structures with varying doses of illumination. Lithography techniques have their limitations in terms of structure depth, particularly for Fresnel lenses with large depths. It is Diamond turning the technique which is preferred for such applications, and it has been used to fabricate Fresnel structures on metals like oxygen-free copper and electroless-plated nickel. The fabrication of Fresnel structures on brittle crystalline materials like Ge is an elaborate process, because Ge is difficult to machine due to its brittleness at room temperature. It is important to mention that plastic deformation can occur in Ge during micro indentation, scratching, and machining tests without brittle fracture. This plastic deformation happens because of high-pressure phase transformations. These findings have given us a good understanding into the physics of micro deformation mechanisms and have contributed to the development of ductile regime machining technology for Ge. The critical undeformed chip thickness required to achieve a completely ductile-cut surface on Ge substrates with different crystal orientations is approximately 60nm [40]. The micro grooving method has also been proposed for fabricating infrared Fresnel lenses on Ge using ductile-mode diamond turning. This method enables the production of various types of micro Fresnel structures on hard brittle materials [41].

4.2.4 Ge based mid IR photonic integrated circuits

Ge based active devices have been developed alongside Si passive photonics circuits. Even though it was focused on Telecom and Datacom applications in the near-IR at the beginning this development has now triggered scientists' interest in longer wavelengths in the mid-IR range. While Si is transparent up to 8 μm wavelength, the strong absorption of SiO₂ puts limits on the operating wavelength range of conventional SOI waveguides beyond 4 μm . In order to overcome this, new strategies have been developed, including optimized designs of SOI waveguides to reduce the overlap with SiO₂ cladding [42]. The other options are using engineered Si membranes with sub-wavelength grating nano-structures to achieve air-cladded Si waveguides by using Si nanopillars [43], or adopting Si on Sapphire configurations [44]. But the development of Si based mid-IR photonic circuits and their limits have made Ge a suitable for extending the operating wavelength of Group IV-based photonic integrated circuits beyond 8 μm , potentially reaching 15 μm . We have to mention that Ge has a strong third order nonlinearity, which has many advantages for the development of active devices. So, as we understand the main purpose is to create photonic platforms dedicated to longer mid-IR wavelengths, primarily based on Ge or SiGe alloys. The characterization of waveguide propagation losses make it possible to assess the potential practicality of each platform. Passive photonic devices have been developed as fundamental building blocks for future mid IR photonic integrated circuits, and on chip resonators are now a necessary part of on-chip sensing, spectroscopy, and nonlinear optical functionalities [45].

4.3 Ge for photovoltaics' fabrication

High-efficiency solar cells are commonly fabricated on Ge and GaAs substrates and each one has its unique cell designs. We have to point out that they were at first developed for space applications. These cells are finding practical applications on Earth more and more during the last years and mostly in high light concentration systems [46]. Ge junctions are very important in PV and TPV applications. A typical Ge cell can generate as calculated 50 mA/cm² under 1 sun with an AM1.5 spectrum and it features a Voc of approximately 250 mV [47]. Ge is often used as a bottom cell in a two terminal triple junction device, whether in 1 sun, concentration, or as a standalone cell in TPV setups, where incident radiation density is above the AM1.5 standard. This setup makes it possible for a Ge bottom cell to amplify

the triple junction cell's efficiency with the increase being from 3% up to 4% measured with absolute values. The current technology for the manufacturing of Ge cells involves dopant diffusion, starting from either an n-type or p-type substrate. This diffusion procedure has a disadvantage: it gives us broad dopant profiles and not sharp junctions. This results in the demand for accurate experimental control in order to gain correct reproducibility as well as controlled doping profiles. Homoepitaxy of Ge on Ge substrates can provide us with a potential solution in order to get the desired PV conversion performance and give greater freedom in the structural design by controlling layer thickness and dopant incorporation. When the dopant elements become diffused from an epilayer then the pre-growth parameters, surface preparation, nucleation layers, and overall layer quality influence successful and reproducible diffusion of elements into Ge. Current matching amongst different cells is pivotal in multi junction solar cells, as they are connected in series, restricting the total current to that of the lowest photogenerated current of all cells. We have to mention the observation that in standard triple junction solar cells, the Ge subcell is not the component that puts limits on the performance. GaAs as well as InGaP produce current densities that vary between 15-20 mA/cm². But, Ge can generate over 40 mA/cm², making this way the bottom cell overrated. The best available Ge cell can contribute up to 240 mV to the device's open circuit voltage. The property the Ge cell has that the current density well exceeds the current matching constraint has paved the way for innovative bottom cell designs alongside with the development of epitaxial MOVPE Ge technology.

Some different cell designs have been promoted which include depositing a double Ge bottom junction to divide incoming light and photogenerated current between two identical cells, effectively doubling Ge's Voc contribution. Another option that has been proposed is to add a Bragg mirror before the bottom cell to reflect unabsorbed photons or photons generated by radiative recombination. Some of the triple junction configurations no more use a Ge bottom cell at 0.67 eV in order to make use of a more optimized 0.89/1.32/1.83 eV bandgap combination exploiting lattice-mismatched In_{0.37}Ga_{0.63}As, In_{0.04}Ga_{0.96}As as well as InGaP junctions. This kind of cells which are grown on GaAs in an inverted design, have achieved optimal performance. One of the highest performances achieved is 41.1% [48]. With these condition a Ge substrate or layer is not needed anymore. In an attempt to achieve lower costs and lower defect density due to heteroepitaxy growing a Si_{1-x}Ge_x layer on Si, with x moderately rising from 0 to 1 has been proposed [49]. Then a Ge layer can be coated onto Si with

reduced defect density. Virtual substrate technology has been developed to create Ge/Si_{1-x}Gex/Si structures with promising results for GaAs solar cells. Epitaxial lift-off processes also offer potential substrate recycling opportunities.

Chapter 5

Development and future perspectives

5.1 Moore's law

The planar Si transistor was the state of the art innovation that resulted in the development and understanding of ICs. The frantic pace at which the ICs circuits developed even from the first years of their invention changed the way we live radically. This has led to people living during the 21st century in developed countries being unable to even imagine how life would be without smartphones, PCs, etc. Today the electronics' market clients have become more demanding than even making the electronics industry worth trillions of dollars. The ongoing drastic development of ICs was observed by Gordon Moore in 1965. Gordon Moore was a Ph.D. chemist and an insightful researcher at Johns Hopkins University and later at Shockley Semiconductor Laboratory. He was also the co-founder of Intel. His prediction was not a proven theory in the the sense we understand proven theories in science. It was an observation made by him.

5.1.1 The first years: from the observation in 1965 to the amendment in 1975

The exponential growth in electronics was predicted by the empirical observation known as Moore's law. Moore was asked by Electronics Magazine to comment on the advance of the electronics industry in 1965. In the 35th anniversary issue of this magazine and only six years after the fabrication of the first transistor that could be put into massive production and sold in the electronics market, Gordon Moore published his empirical observation. It was simple to

understand but at the same time really important and it somehow defined the semiconductor industry for the next years. He stated that the number of components (components in general and not transistors in particular) that were fitted in a chip was about to approximately double every year. We can see the plot of this observation in Figure 5.1. By the term components he meant apart from transistors, capacitors and resistors [50]. The progress of the semiconductor industry for about ten years and the number of components in the chips that could be commercialised made Moore reconsider his initial prediction. He amended his statement by saying that the number of components per chip was about to double every two years as shown in Figure 5.2. He went on to revise his initial prediction when he noted the number of components in the most up to date charge coupled device memory which was fabricated by Intel and whose memory chip consisted of 32,000 components and 16,000 transistors. The exponential growth in the number of components fitted per chip was achieved by the thorough improvement of three key factors: the reduction of the feature size, the increase in the chip area and the enhancement in the circuit designs as well as the device's overall fabrication. By noticing these three factors he was able to publish his amendment on his law in 1975. But we have to mention that he clarified that his slope was not about to change immediately but would take 5 years approximately to do so. That was because of the CCD memories Intel was working on and the way Moore counted their components. Even though the doubling of the components every year was no more possible by the chips which were commercialised after 1975 -for example the 64kb DRAM chip which should have been fabricated in 1976 by following the initial statement, was finally commercialised in 1979- the 1975 statement of doubling every two years was rather pessimistic [51].

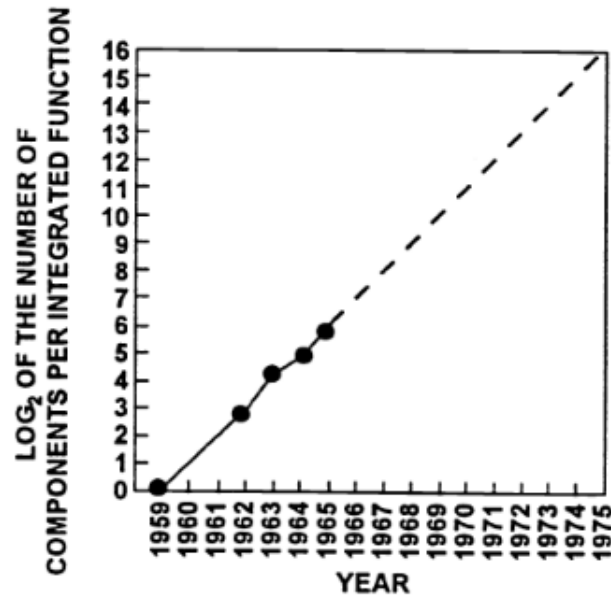


Figure 5.1: The initial prediction by Gordon Moore in 1965 plotted [51].

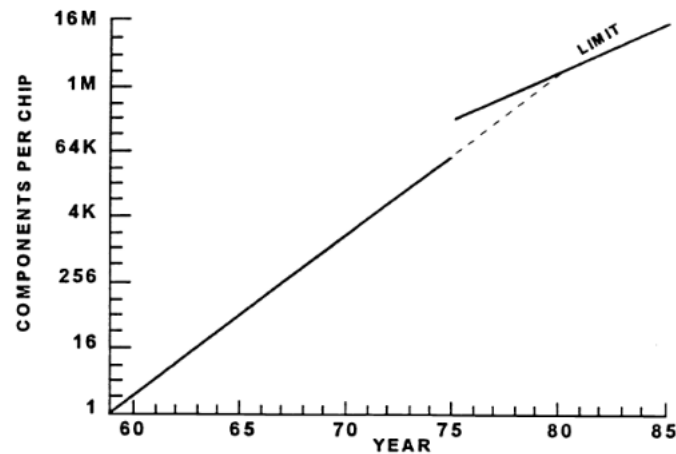


Figure 5.2: Moore's 1975 amendment [52].

5.1.2 Actual progress after 1975

His retelling of the story in 1975 proved to be too pessimistic compared to the previous one but optimistic as well at the same time. It is clear that the deceleration was already implemented in 1975 since Intel never put into mass production its 16kb CCD memory chip because it was prone to irradiation. But, his statement that the number of components was about to double every two years was not that precise. The reason of this failure was because he predicted an annual enhancement in circuit density of 50% but in fact it was close to 60%. The

industry followed a doubling of transistors per chip every 18 months during the next years. We have to note here that they changed from counting the components to counting the transistors per chip. The chips that were commercialised after 1979 followed a doubling of transistors every 18 months [52]. But before 1980 Moore's law was somehow dichotomized. Memory chips and logic chips followed different ways of advancement. Memory chips' progress complied with Moore's law as opposed to logic chips mostly microprocessors which had a remarkably slower progress as shown in the plot of Figure 5.3. Until 2000 memory chips consisted of more or less 1 billion transistors. This was an extraordinary number for logic chips since they contained 20-40 million transistors each depending on the chip. The number of transistors per chip (memory or logic) demonstrate how necessary the amendment of Moore's law was since memory chips saw an increase on the number of their transistors 58% and logic chips 38%. Moore's law continued to be in use during the 21st century with its ups and downs [53]. The actual progress made until 2022 can be seen in Figure 5.4. As we are approaching the physical limits due to the fixed size of Si atoms scientists try to find other paths to keep the law in use. But, remarkably the law has begun to slow down.

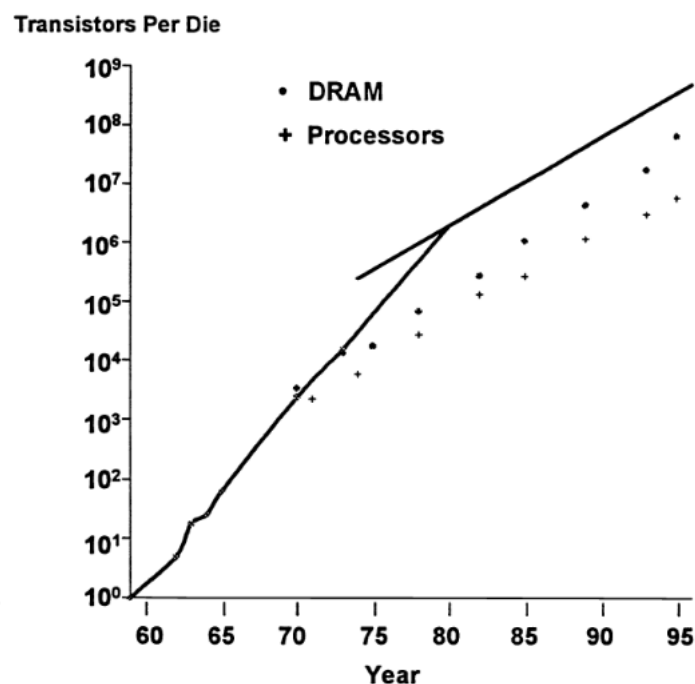


Figure 5.3: Actual transistor count until 1995 compared to Moore's 1975 amendment [52].

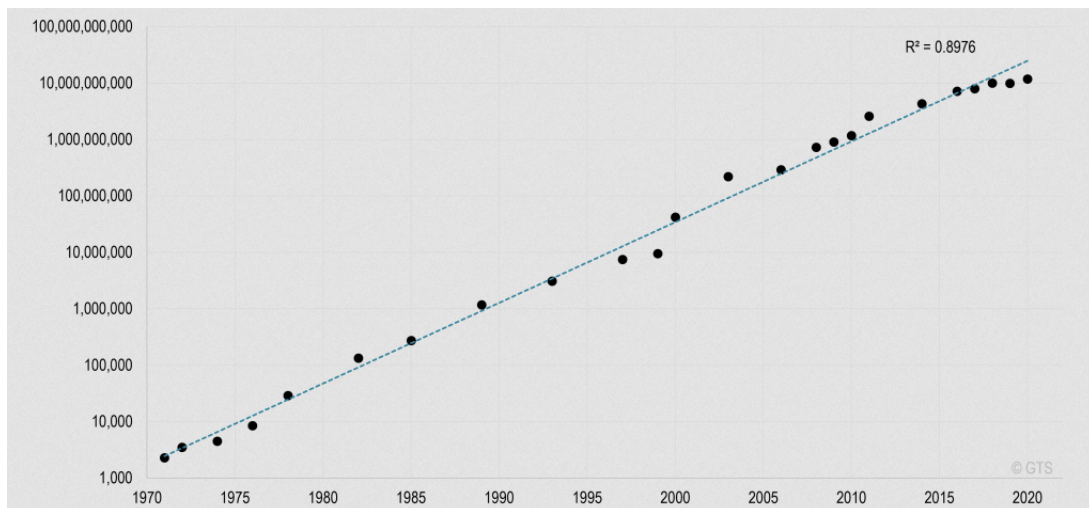


Figure 5.4: Moore's law actual slope up to 2022 [54].

5.1.3 Moore's law reaching physical limitations and future challenges

The term transistor count refers to the number of transistors per chip. As for now the biggest transistor count ever achieved is 134 billion transistors which are fitted in Apple's ARM-based dual-die M2 Ultra system on a chip. There has been a controversy during the last years regarding Moore's law. Some believe that the law will be dead soon due to the limits physics impose. Some others state that the law is still applicable [55]. To be more specific, about one year ago, in September 2022 the CEO and cofounder of Nvidia -which is one of the companies now dominating the semiconductor industry- Jensen Huang made the statement that Moore's law is now dead. Pat Gelsinger who is Intel's CEO stated exactly the opposite meaning that Moore's law is still alive and there is further possibility of packing even more transistors into a single chip. The law has been applicable during the last 58 years because of the continuous shrinking of the size of transistors. But Si atoms have a specific size. It is clear that we cannot manufacture transistors that are smaller than the size of a Si atom. Indicatively, IBM is working on transistors that are just one order of magnitude bigger than one Si atom. But, this is not the only problem. Moore's law is not only about the number of transistors packed in each chip but also the cost of each chip. As the size of transistors shrinks, the cost of semiconductors drops. This is not about to continue to happen because as we are approaching some physical limits the cost of cooling and fabricating transistors starts to rise. Some scientific factors to take into consideration for the future transistors (mainly CMOS) are:

Thermodynamic limits

Memory cells are the basic units of storage in computational systems. Memory cells are the ones that possess the information, basically in the form of bits. They have different states that represent distinct pieces of information. The most known states are binary but we also have the multi level ones. In order for computing process to have the right outcome, the changes made to memory cells should be distinct and recognizable and give the system the ability to interpret and process the data correctly. When performing computation, the operations carried out on memory cells should result in a permanent and distinct change. This means that the change that takes place has to be reliable and not easily reversed or if it is possible not at all under any circumstances. These are the main factors that affect useful computation operations. Thermodynamic entropy is the measure of randomness in a system. It is profound that when the states of memory cells are changed we need to consume energy to achieve that. The formula $S = k_B \ln(m^n)$ indicates how much disorder increases when we change (n) memory cells among (m) possible states with (k_B) being Boltzmann's constant. In order to thoroughly describe the thermodynamic entropy we need to refer to the second law of thermodynamics which is described by the formula $S = Q/T$, and from which we understand that entropy (ΔS) is related to the energy spent (ΔQ) as well as temperature (T). So, the energy needed to write information into one memory bit (Ebit) is given by the formula $E_{bit} = k_B T * \ln 2$. Again we have the Boltzmann's constant (k_B) and (T) which is the surrounding environment's temperature. The deduction from the above is that in order to work out a single bit at the temperature of 300K 0.017eV is the minimum needed [56]. As far as the minimum feature size is concerned, we have to refer to another principle known as Heisenberg's uncertainty principle which says that it is impossible to simultaneously know the speed as well as the position of a subatomic particle such as an electron, $\Delta x \Delta p \geq \hbar/4 * \pi$, where ($\hbar$) is Plank's constant, (Δx) is the uncertainty in position, (Δp) is the uncertainty in speed and (π) is equal approximately to 3.14, we conclude that the smallest size for an electron carrier is about 1.5nm. We need also to point out that the power needed per unit area if we consider the packing density of memory cells, is about $3.7 MW/cm^2$. If we want to make a comparison we need to mention that the surface of the Sun receives only $6000 W/cm^2$. But, the limits are going to be more precisely calculated after we consider the phenomenon of tunneling.

Quantum tunneling

In quantum mechanics, quantum tunneling can be described as the possibility of particle being in a state that is not allowed in the classical mechanics. The particle can be an electron that overcomes an energy barrier which theoretically it could not when classical mechanics are considered. When the electron goes over this barrier this phenomenon is called thermionic injection which is described by the equation $GT = \exp(-Eb/kBT)$, where (GT) is the likelihood for thermionic emission to take place, (kB) is the Boltzmann's constant as it was in the previous formulas, (T) is the temperature of the material and (Eb) is the energy barrier that the electrons need to surpass. When the electron goes through the barrier then we have the phenomenon of tunneling which is described by the equation $GQ = \exp(-2a2mE/(h/2 * Pi))$, where (GQ) is the probability of tunneling, (a) is the width of the possible barrier, (m) is the mass of the particle that is possibly going to undergo tunneling, (E) corresponds to the energy the particle has before tunneling and h the Planck's constant. In order to perform useful computation the two states in which the electron can get into need to be discernible. The error in distinguishing them has to be as small as possible. By limiting the error we can get the minimum energy barrier so that the two electron states can be distinguished. The equations are not mentioned because this is far from the goals of this thesis. The maximum power needed for successful computation (Pmax) is described by the equation: $P_{max} = f * (n/A) * [kBT \ln 2 + ((h/2 * Pi) \ln 2)^2 / (8ma^2)]$, where (A) is the area of the barrier of tunneling, (n) the number of devices in this area and (f) the frequency at which the devices operate, kB the Boltzmann's constant, (T) the temperature, (h) is Planck's constant, (m) the mass of the particle that is going to tunnel and (a) the width of the barrier [57].

Thermal limits

When increasing the power of a chip one of the most significant challenges is to avoid the overheating of the chip. Most chips that are manufactured now can sustain approximately up to 400K. Another factor that affects the allowable limits of power increase is the speed at which heat can be removed from a typical chip. When we talk about removing heat from a chip we have to refer to Newton's law of cooling which describes the way heat is removed. The formula of this law is $Q = H(T_{Dev} - T_{sink})$, where (Q) is the total amount of heat which is taken away from the chip, (H) represents the heat transfer coefficient whose value depends on the properties of the material used, (TDev) is the temperature of the chip and

(T_{sink}) the temperature of the chip's surroundings [58]. From the equation it becomes clear that the heat taken away from the chip depends on the temperature difference between the chip and its environment. So, when the chip's temperature is lower ($T_{\text{Dev}} < T_{\text{sink}}$, T_{Dev} refers to the chip's temperature and T_{sink} to the temperature of its surroundings), it is better for the energy required to process a bit (Ebit). But Carnot's theorem, which was formulated to describe heat engines, tells us that the work which is required to take away heat increases with the temperature difference. This affects the total energy required for computation. The total energy needed for computation includes the original Ebit and the additional energy required to perform heat removal. The formula is not mentioned because this is far from the goals of this thesis. We have to mention that for features which are less than 1nm, power requirements are extremely high and the same happens but in a lower scale with features which are below 2nm. But as feature sizes get smaller, Ebit and power behave better at higher temperatures compared to lower temperatures [57]. From the above, we can conclude that increasing the power of a chip, avoid overheating while at the same time make the chip's features as small as possible is a complex challenge.

Compton wavelength

The continuous shrinking in the size of transistors is facing many engineering and physics challenges and some of them we have already analysed in the previous paragraphs. We could also mention current leakage, thermal noise etc. If we overcome these problems then it is believed that quantum mechanics and in particular Heisenberg's uncertainty is going to form the final limit on how small transistors can get [59]. While today transistors are mainly Si based a lot of research focuses on single electron transistors (SETs). In SETs the electron is the component of the transistor which is the smallest and not the Si atom. So, in this case Heisenberg's uncertainty is going to put the final limit in transistor's size. Electron's invariant mass is about 9.1×10^{-31} kg. The Compton wavelength which is the measure of the size of an electron, for a single electron is about 0.00243nm [60]. It is controversial if we will be even able to overcome all the other engineering challenges and even approach this limit. This is because at lengths around the Compton wavelength which is an extremely tiny scale, the power needed and the energy per bit (Ebit) required for computations start to increase uncontrollably. This massive increase indicates that when we approach this extremely small scale, the computational requirements become very impractical.

5.1.4 Possibility of Ge being used for next generation transistors

Since Si is expected to overcome the physical limits soon especially after 5nm transistors were introduced, scientists and engineers are now investigating different channel materials that could replace Si in the future. The Taiwan Semiconductor Manufacturing Company which is also one of the companies now dominating the semiconductor industry was the first to fabricate transistors with SiGe being the channel material instead of Si. Since SiGe channel PMOS transistors were manufactured there has been an improvement of approximately 18% in the performance compared to Si channel transistors. It is obvious that research on Ge as a material for transistors' fabrication has been motivated by many factors with the most important one being the continuous miniaturisation of transistors and finding ways to not stop improving computing power while at the same time reducing the cost of electronic devices. Since Ge obtains a comparatively to Si higher holes and electrons mobility, it could possibly lead to faster and more efficient NMOS as well as PMOS transistors.

5.2 CMOS technology overview

The need to make ICs consume as less power as possible and make them noise immune brought the Complementary Metal Oxide Semiconductor (CMOS) technology. Today, CMOS is the most widely used technology in ICs. But before explaining the principles of CMOS lets take a closer look at PMOS and NMOS transistors:

1. NMOS: An n-channel MOSFET is composed of an n-type drain and source which is diffused on a p-type substrate. As we have already mentioned in n-type semiconductor materials the majority carriers are the electrons. The NMOS conducts electricity only when adequately high voltage is applied to the gate terminal of the transistor. It is easy to understand that NMOS transistors are clearly faster than the PMOS ones since holes are slower than electrons.
2. PMOS: On the opposite, p-channel MOSFET has a p-type source and drain which are diffused on an n-type substrate. Here, we have the holes as majority carriers. In order for PMOS to conduct a low voltage must be applied. As opposed to NMOS, PMOS do not conduct electricity when high voltage is applied to the gate terminal.

The CMOS technology utilises both of the above mentioned types of transistors. If we

want to give a general description of how they work, we would say that they work in pairs (NMOS-PMOS) in a complementary way. In particular, the pairs of the NMOS-PMOS transistors' arrangement allows, the one transistor to conduct current and be in on mode when the other one is switched off and as a result is not conducting current. With this arrangement current flow is prevented and thus we have less power being consumed.

5.3 Ge MOSFET

The main reason why interest in Ge has been restored when trying to find new materials in order to keep electronics' exponential evolution is that it has certain physical properties that make it more suitable than Si for nanoscale applications. In Ge electrons and holes move more easily through the material when an electric field is applied. This is because of the lower effective masses of electrons moving sideways and light holes as well as heavy holes. This characteristic is what makes Ge more suitable than Si for highly miniaturized MOSFET applications even when considering Si's saturation velocity which is clearly higher. The comparatively more balanced mobility of electrons and holes in Ge not only allows the fabrication of smaller p-MOSFETs but also enables the creation of additional CMOS logic gates. We have to mention that Ge has a melting point lower than that of Si and this presents the possible ability of creating Ge MOSFETs using processes with significantly lower heat requirements. It is highly controversial if Ge, on its own, will ever be the primary material for constructing ICs [61]. What is more likely from how technology is evolving up to now is that it may need to be combined with Si through heterogeneous integration. So one possible scenario is that Si devices will be manufactured first, followed by the integration of Ge such as Ge PMOS integrated with Si NMOS in a three-dimensional arrangement or for incorporating optical devices with CMOS. The limited thermal budget available for Ge in these cases makes its integration more manageable. The compatibility of most high-k dielectrics and metal gates with Ge is generally better than with Si. The less favorable qualities of Ge oxides as opposed to SiO₂ make this dielectric less suitable for insulating and isolating Ge MOSFET gates, which has made nearly impossible large-scale integration in Ge for many years. It becomes clear that for Ge to become widely used, the integration of crystalline Ge layers onto Si through heterogeneous methods is important to be implemented.

5.3.1 Understanding the need for a new channel material in MOSFETs

Finding an alternative channel material has been the main target during the last years because it is important to enhance the drive current of the next generations of transistors as well as to minimise the power drain. Another reason behind the efforts to find new channel materials is the need to increase the switching speed of the transistor. When we have a transistor with a comparatively extensive channel length, the charge carriers scatter multiple times during their transition from source terminal towards the drain terminal and as a result they end up with speed repletion. But, when the channel length is no more than 100nm, the injected carriers have the ability to cross the whole channel without hitting velocity repletion. In order to achieve a higher drive current we need to increase the injection speed and minimise the back scattering rate as much as possible. For this purpose, we need a material which will have a decreased carrier effective mass. The material's mobility is inversely proportionate to the effective carrier mass. It becomes clear that substituting Si with a material which has an increased mobility will rise the transistor's drive current. Materials like InAs and GaSb have been proposed to substitute Si as a channel material. But, Ge's mobility of holes is significantly higher than that of the above mentioned materials. We have to mention that Ge's mobility of electrons is 2.5 times greater than that of Si. Since in Ge the charge carriers' mobility is comparatively high as well as balanced, it is the most suitable material to substitute Si for high performance MOSFETs fabrication. Another significant factor is that Ge's techniques for processing are similar to those of Si and as a result it can be used by the existing industry immediately without radical changes in the existing manufacturing technology. This can be understood by the adoption of SiGe in the PMOS channel.

Even though GaAs as well as other semiconductor compounds that are formed from the combination of the chemical elements of the Group III and the Group V of the periodic table have a relatively high electron mobility, their insufficient effective mass makes them inappropriate when elevated electron carrier concentration is needed. They have also difficulty in achieving high drive currents. Another obstacle that prevents them from massively replacing Si is that their leakage current during off-state is higher than that of Ge. The reason why scientists are still skeptical about Ge replacing Si in the electronics industry is that although the high charge carrier mobility Ge has, it has certain drawbacks that prevents it from dominating the semiconductor industry. With Ge it is hard to achieve adequate defect passivation which is important for the gate oxide interface. Defect passivation is necessary because it

neutralises defects within the semiconductor material which arise during the fabrication process due to impurities in the material. The gate oxide interface when a MOSFET is concerned is the boundary amongst the gate electrode and the thin insulating layer which is the oxide that isolates the gate electrode from the underlying semiconductor substrate [62]. Also, in Ge transistors it is hard to minimise the leakage current. These disadvantages result from its low bandgap. The inability to reach high drive current in NMOS transistors made of Ge prevents the evolution in Ge's CMOS technology.

5.3.2 Growing Ge layers on Si substrates heteroepitaxially

It is possible for Ge to take its place in the semiconductors' industry, if we integrate it with Si substrates. Heteroepitaxial growth of Ge on Si results in a significant lattice mismatch which is approximately 4.2% and poses challenges for successful growth, resulting in undesirable outcomes like islanding and misfit dislocations at the interface between Si substrate and the Ge film. The misfit dislocations that are caused by the relatively high lattice mismatch result in threading dislocations on the surface of the film. This has negative consequences on the device's effectiveness. In order to overcome these obstacles, an approach named Multiple Hydrogen Annealing for Heteroepitaxy has been developed. This technique involves a procedure of two main steps. At the first step a thin Ge film is deposited on Si through CVD method at a temperature of more or less 400°C. At the second step a higher temperature of approximately 825°C in situ H₂ heat treatment takes place. This procedure significantly drops the roughness of Ge surface by 90%, bringing it down to 2.5nm rms. This process is revised as many times as needed to achieve the preferred thickness. MHAH technique achieves successful growth of high quality heteroepitaxial Ge on Si with the least possible defects. Defects are mainly restricted around the Si/Ge interface, forming smooth single crystal layers of Ge on Si substrates. The threading dislocation count is limited to $3 * 10^6 cm^{-2}$, with a surface roughness which is no more than 0.7 nm rms. This technique not only limits the defects in a specific area but also allows for deposition of Ge layers of high thickness on Si through the SiO₂ windows. Ge film does not grow both on Si and SiO₂ but only on Si. But, we have to mention that this procedure can be implemented if we want to grow lateral Ge films on the surface of SiO₂. This results in Ge on insulator setup with over lateral films. In this setup, the threading dislocation density is around $10^6 cm^{-2}$. The applications of this method are broad, including the high mobility Ge only channel MOSFETs being heterogeneously

integrated directly onto Si substrates [63]. This technology advancement holds promise for the next technology evolutions.

Chapter 6

Conclusions

6.1 Summary

In this thesis, we tried to figure out whether there is a possibility for Ge to substitute the up to date dominating Si in the semiconductors industry. Even though during our discovery phase it became clear that the abundance of Ge on the Earth is far less than that of Si, in the bibliography they do not usually pose this reason for Si being almost exclusively used. However, we have to mention that the comparatively lower cost of Si is frequently mentioned as one of the reasons why it overshadowed Ge just seven years after the first ever transistor was fabricated which was made of Ge. If we could summarise the factors that led to Ge's replacement those would be the higher energy gap Si has which means that for electrons in Si atoms it is far harder to enter the conduction band by overcoming the energy gap which in simpler words means that Ge crystals have more free electrons than Si crystals when compared at the same temperature. Another reason is the Si's advanced temperature stability which means that heat does not damage its devices as easily as it happens with Ge. Also, Si possesses large forward current and high reverse breakdown voltage.

From 1965 until now Moore's law -which is more an act of will than a law- has been driving the transistor density per chip. However, as we are approaching the physical limits of Si devices, a lot of investigation is conducted in order to find new materials for transistors' manufacturing. Ge is a candidate channel material for high performance MOSFETs due to the relatively low pre-load Ge requires. It is still controversial if Ge will be used alone for high performance MOSFETs or if it is going to be heteroepitaxially grown on Si surfaces.

6.2 Future extensions

This thesis could be an inspiration to investigate other semiconductor materials as possible substitutes of Si. By analysing their properties, behavior etc theoretically as well as practically there could be useful conclusions regarding the future of semiconductors and how we are going to keep the computing power of our devices increasing while at the same time dropping their cost. In August 2023 the base metal and critical mineral exploration company Rockfire Resources PLC confirmed that there is Ge deposit in the mine of Molaoi in Lakonia, Greece. This means that our country is now at first place as far as Ge mining is concerned. Investigations on the quality of the mined material are being conducted and will continue in order to figure out how to reclaim the deposit[64].

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