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Morphological Study of SiGe Solid Solution Growth Epilayers

Maher Nadher Abdullah

Mathematics Department -Al-Muqdad Collage of Education - University of Diyala

maherm@uodiyala.edu.iq

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Abstract

In this research, the procedures were obtained for the growth of epilayers of $Si_{1-x}Ge_x$ solid solutions from tin and gallium solution-melt. The two solutions of the molten material were dissolved on a single-crystal silicon substrate in the direction of <111>. To reduce the amount of solution-melt used, the epitaxial layer was developed from a minimal volume of solutions of tin (Sn) and gallium (Ga) melt in a hydrogen atmosphere that had been purified by dissolving palladium (Pd) and was constrained by two substrates. The results were to obtain the lowest dislocation density in thin films. The relationship between thin film dislocation density and thickness was an exponential relationship between its variables. Thin films with a compound containing a smooth structure change were obtained by smoothly changing the lattice parameters of the gradient gap solid solution, and a structure of epilayers of gallium on a silicon substrate was also obtained.

Keyword: Thin films, Solid solution, and Dislocation.

دراسة مورفولوجية النمو الطبقي الفوقي لمحلول SiGe الصلب

ماهر نادر عبدالله

قسم الرياضيات – كلية التربية المقداد – جامعة ديالى

الخلاصة

في هذا البحث، تم الحصول على نتائج لنمو الطبقي الفوقي المحوري لمحلول $Si_{1-x}Ge_x$ الصلب من محلولي انصهار القصدير و الغاليوم ، و تم صهر المحلولين من المادة المنصهرة (القصدير و الغاليوم) على الركيزة السيليكون أحادية البلورة

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باتجاه <111> . من أجل تقليل كمية المحلول الذائب المستخدم، تم تطوير و تحضير الطبقة الفوقية المحورية من حجم صغير جدًا من محلولي انصهار القصدير و الغاليوم في جو هيدروجيني تم تنقيته بواسطة البلاديوم وتم تقييدها بواسطة دعامتين للتثبيت. كانت النتائج هو الحصول على اقل كثافة انخلاع للاغشية الرقيقة المحضرة. كانت العلاقة بين كثافة الانخلاع الاغشية الرقيقة المحضرة و سمك الغشاء الرقيق المتكون خلال علاقة اسية بين القيم المتغيرة لها. تم الحصول على اغشية رقيقة ذات متراكب يحتوي على هيكل سلس متغير و ذلك عن طريق التغير السلس لمعلمات الشبيكة للمحلول الصلب ذو الفجوة المتدرجة و أيضا تم الحصول الهيكل الفوقي المحوري مثالي من محلولي القصدير و الغاليوم المترسب على ركيزة السيليكون أحادية البلورة.

الكلمات المفتاحية: الأغشية الرقيقة ، المحاليل االصلبة ، كثافة الانخلاع.

Introduction

One of the ways to obtain epilayers in semiconductor instrumentation is their crystallization from solution-melt, called liquid-phase epitaxy (LPE), which makes it possible to get them with different contents of composition components[1].

The solvent can be a melt of one of the main components of the crystallizing compound and a solid solution, for example, a melt of gallium in the preparation of $Si_{1-x}Ge_x$ epilayers . It can also be a melt of a low-melting alloying element, for example, a tin melt in the preparation of tin-doped $Si_{1-x}Ge_x$ epilayers [2].

To create semiconductor devices, heterostructures based on a solid solutions of compounds of the class A^{IV}–B^{IV} are used. Two-component solid solutions have the feature that it is possible to preserve a crystalline structure while varying band gap (*Eg*) and crystal lattice period (a) of the films in a smooth and insignificant change along the direction of growth. However, semiconductors and heterostructures based on them of this class usually have a significant drawback, consisting of a mismatch between the lattice parameter (*a*) (a_{Si} = 5.4307 Å, a_{Ge} = 5.66 Å) and the coefficient of thermal expansion (α) (CTE) ($a_{Si} = 5.1\times10^{-6}\,K^{-1}$, $a_{Ge} = 6.1\times10^{-6}\,K^{-1}$) of the substrate and crystallized layer. Because of this, many defects are formed in the film [3].

When two- and multicomponent solid solutions are grown from the liquid phase, the following factors play an important role in the formation of defects: The compositional inhomogeneity along the thickness of the epilayers , *dC/dx*; and the difference between the lattices period Δ*a* and CTE Δ*a*, conjugated at the material interface. Defects in two- component heterostructures are also heavily influenced by the substrate defects inheritance. Charge carriers dissipate defects, drastically worsening the properties of semiconductor devices built on their foundation [4].

To obtain a heterostructure matched in terms of the crystal lattice period and CTE, it is necessary to transition to two-component, smoothly varying graded-gap compositions of solid solutions.

The use of $Si_{1-x}Ge_x$ semiconductor solid solutions grown on silicon substrates makes it possible to control the band gap *Eg*, lattice period *a*, and CTE α, which is especially important for devices based on radiative recombination[5].

The investigation of $Si_{1-x}Ge_x$ solid solutions grown on silicon substrates is highly pertinent in this respect. The band gap and photosensitive spectral area of the $Si_{1-x}Ge_x$ solid solution can be controlled by gradually altering the composition. When Si and Ge are combined to form solid solutions, for example, the solid solution's band gap spans a wider spectral photosensitivity range than the spectral responsive regions of Si and Ge. This is crucial for the production of solar devices and acts as a buffer layer for the formation of structures like $Si\text{-}Si_{1-x}\,Ge_x\text{-}(Ge_2)_{1-x}\,(GaAs)_x$, $Si\text{-}(Si_2)_{1-x-y}\,(Ge_2)_x\,(GaAs)_y$. In addition, for the intensive development of microelectronics, semiconductors are needed with much higher breakdown electric fields than of silicon (Si), band gap, higher electron mobility, and high-temperature resistance [6].

V. Timofeev et al. [7] studied at a growing temperature of 150 °C, the critical transition thickness for two- to three-dimensional growth has been determined for Ge-Si-Sn films with a constant Germanium substance and a Tin substance that varies from 0 to 16%. Diagrams of phase for the superstructure shift that occurs as Tin grows epitaxially on silicon and germanium (100) were constructed. It is possible to control the Sn segregation on the superstructure

identified by the reflection high energy electron diffraction (RHEED) image and determine the Tin layer on the silicon substrate using phase schematic data.

According to the research study by E. Mathe et al. [8] thin crystalline films $Si_{1-x}Ge_x$ were created by intensely irradiating (2.5×10^{16} ions/cm^2) implanted Ge <100> Si with an (ArF) excimer pulsed laser. Through solidification and melting procedure that occurs both during and after the laser discharge, the layer that was rendered amorphous by implantation begins to crystallize. Investigations have been done on both completed structures and the partial melting of the entire amorphized layer. The findings also demonstrate how more pulses cause grain to grow.

The researchers S. Matveev et al. [9] used molecular beam epitaxy to produce $Si_{1-x}Ge_x$ epilayers on heterojunction silicon and sapphire structures. The sources used were sublimated silicon and gaseous germanium. Because the structural perfection of the layers that formed immediately on sapphire substrates was less than ideal, Si buffer layers were utilized in later growth runs. We identified the concentration-depth characteristics of Ge, Si, and background defects throughout the layers using X-ray photoelectron spectroscopy. The structure of the SiGe layers was shown to be unaffected by changing the buffer thickness of Si in the region of 50–300 nm. At substrate temperatures between 360 and 410°C, single-crystal SiGe layers have been produced. The layers' structure was unaffected by changing the germanium concentration between 5-25%, but their roughness did slightly rise.

The aim of this research is to investigate the methods of deposition and growth in the interest of comprehending the structural characteristics of the formed epilayers of $Si_{1-x}Ge_x$ solid solutions from tin and gallium solution-melt. These two solutions of the molten material were dissolved on a single-crystal silicon substrate in the direction of <111>.

Materials and Methods

We have grown epitaxial films of $Si_{1-x}Ge_x$ solid solution, such as through liquid phase epitaxy (LPE), in a broad concentration range from a limited Sn and Ga solution melt ($0 < x < 1$)

on a single-crystal Si substrate with a diameter of 40 mm and a thickness of approximately 400 μm.The $Si_{1-x}Ge_x$ solid solutions were grown using a vertical quartz reactor and horizontally aligned substrates in an EPOS-type setup as shown in the figure (1).

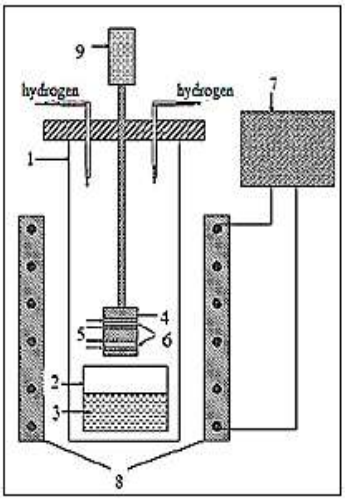

Figure 1: Schematic diagram of the setup for liquid-phase expitaxy.
1- quartz reactor, 2- quartz crucible, 3- solution melt, 4- graphite cassette, 5- silicon substrates, 6- graphite props, 7- control units, 8- thermal units, 9- electric motor [3]

The epitaxial layer was grown from a small volume of Sn and Ga solution-melt in a hydrogen atmosphere purified by palladium (Pd), restricted by two substrates, allowing for a reduction in the amount of solution-melt consumed. First, the reactor was evacuated to a residual pressure of 10^{-3} Pa, and then the heating process started after 25 minutes of pure hydrogen being pumped through the reactor. The equipment switched to the automated mode when the temperature reached the required degree. For 35–55 minutes, the solution melt was homogenized. The correct time was found to stop the growth of $Si_{1-x}Ge_x$ epilayers by centrifugally draining the solution melt from the substrate. The state diagram of the binary alloys Ga-Si, Ga-Ge, and Sn-Si, Sn-Ge enabled the determination of the composite of the solution-melt containing Si, Ge and Ga as well as Si, Ge, and Sn. The solubility of Si in Ge, and Sn was investigated at 450-1150°C to prepare a liquid solution-melt [10]. The $Si_{1-x}Ge_x$ epitaxial films were produced at 1100-500 °C, corresponding to the beginning and finish of crystallization, respectively.

Experiments were conducted with a modification in the necessary parameters to determine how the composition, crystallization onset temperature, and forced cooling rate affect the films' quality. According to studies, the best epitaxial films of the $Si_{1-x}Ge_x$ solid solution can be made by cooling the solution-melt at a rate of 1.5–2.5 degrees/minute, the thickness of the solution-melt being 0.75–1.5 mm, or the width between two horizontally positioned substrates. As substrates, single-crystal Si (111) with n-type conductivity was utilized.

A MIM-8M metallographic microscope was used to examine the surfaces of the produced film's morphology. We have selected the composition of the etchant (we used mixtures of concentrated hydrofluoric (HF), nitric (HNO_3), and (CH_3COOH) acetic, ratios of acids are 1h HF + 3h HNO3 + 4h CH_3COOH). The sample was solution-etched, diluted by deionized water, and then washed to expose dislocation etch pits on the (111) plane. 6-7 counts were made on each layered sample to evaluate the dislocation density (N_D) [11].

Results and Discussion

The experimental results demonstrated that all technological factors, including solvent type, purity, substrate orientation, forced cooling rate, and growth temperature, affect the dislocation density (N_D) of formed $Si_{1-x}Ge_x$ semiconductor solid solutions. We grow gap-graded epilayers where the band gaps (ΔE) vary smoothly from (ΔE_{Si} = 1.13 eV) to (ΔE_{Ge} = 0.66 eV), starting from the Si-$Si_{1-x}Ge_x$ substrate-film boundary, where silicon content declines along the direction of growth, and the germanium content rises.

The observations of a morphological analysis investigation of the surface of four different film samples produced from Sn and Ga solution-melt at the temperature of the start (T_{SC}) and end (T_{EC}) of crystallization are shown in figures 2-3.

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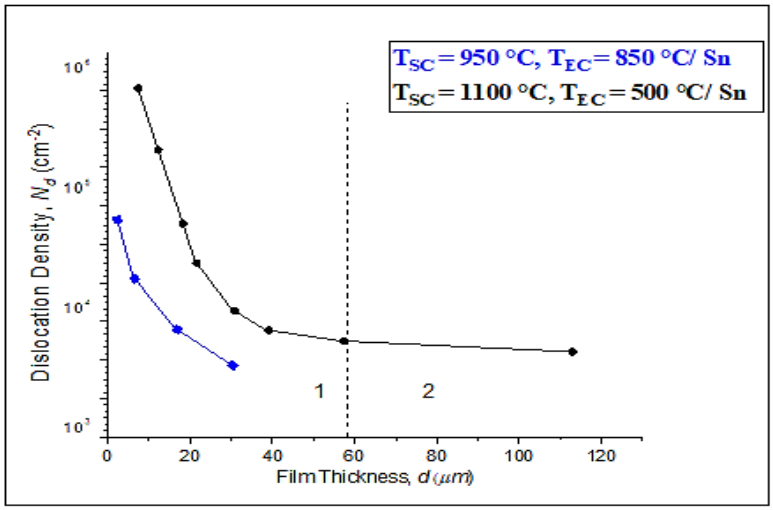

Figure 2: The dislocation density (N_d) of the epitaxial layers of the $Si_{1-x}Ge_x$ solid solution as a function of the thickness (d) of film grown Sn melt solution at different T_{SC} and T_{EC}

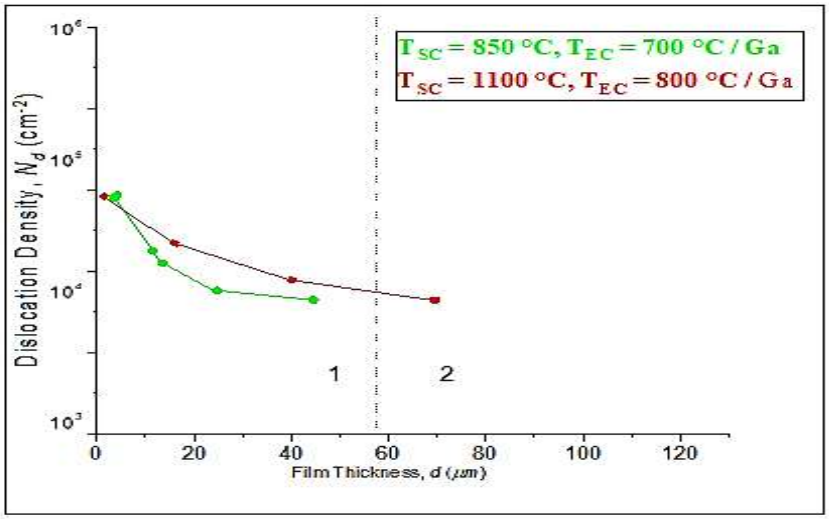

Figure 3: The dislocation density (N_i) of the epitaxial layers of the $Si_{1-x}Ge_x$ solid solution as as a function of the thickness (d) of film grown Ga melt solution at different T_{SC} and T_{EC}

Figures 1-2 show that the relationship between the dislocation density concentration (N_i) of the films and the thickness of the film, and consequently, its composition content in solid solution, is exponential and is given by $N_i=ae^{bd}$ (section 1 in the figures). The coefficients a and b depend

on the content of Si or Ge in the solid solution; then, they are regarded as specific mathematical functions based on the composition of the film:

$a\,(x,y) = (\psi_{i1}x+\psi_{i2}y)\cdot 10^{\gamma}$,

$b\,(x,y) = (\psi_{i3}x+\psi_{i4}y)$,

$N_{i0}\,(x,y) = (\psi_{i5}x+\psi_{i6}y)\cdot 10^{\delta}$, and $\delta > 0 < \gamma$.

The coefficients ψ_{ik} and the degree γ, δ can be (-) or (+) and are determined by experiment (i – sample number (Si). x, y - a solid solution's concentration of Si and Ge, respectively).

Utilizing both experimental results and mathematical calculations, it has been demonstrated that the N_i in the films exponentially reduces in the path of the thickness of the solid solutions, rises to a confirmed value (section 1 in figures 1-2), and then either stays nearly unchanged (section 2 in figures 1-2) or has an unnoticeable linear character to the surface [12].

The functional dependency in this situation is $N_i = N_i\,(d)$ could be expressed through dual analytical formulas on the interval $(0; d_k]$, $N_i = ae^{bd}$, and on the interval $d_k < d$ or $(d_k; d]$, $-N_i = N_{i0}$, where N_{i0} is calculated from the plot using experimental results (see figures 1-2):

S_1: $N_i = 113213e^{-0.092d}$ at T_{SC} = 950 °C of Sn-solvent;

S_2: $N_i = 978843e^{-0.092d}$ at T_{SC} = 1100 °C of Sn-solvent;

S_3: $N_i = 110435e^{-0.043d}$ at T_{SC} = 850 °C of Ga-solvent;

S_4: $N_i = 135978e^{-0.032d}$ at T_{SC} = 1100 °C of Ga-solvent;

The distribution profile of the constituents over the depth of the epitaxial layer was established using the results of the X-ray microprobe analysis. Figures 3-4 show how epitaxial Si layers are first grown on the Si substrate and that their content gradually decreases along the direction of growth. In response, the Ge content increases up to the film surface (this is made possible by the small volume of melt solution), forming a $Si_{1-x}Ge_x$ solid solution based on the growth mode. By varying the temperature of the start (T_{SC}) and end (T_{EC}) of crystallization of the grown solid

solution, we obtain $Si_{1}–xGe_{x}$ films of different thicknesses, which have different degrees of variability (Figure 3-4).

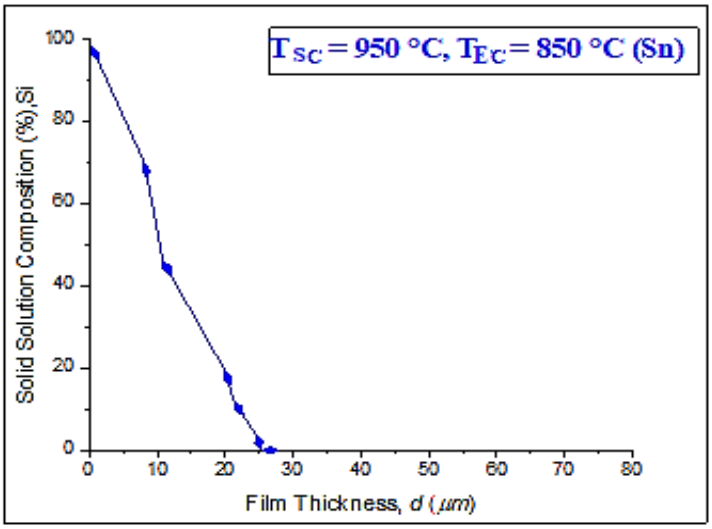

Figure 4: The Si_{1}-$_{x}Ge_{x}$ solid solution composition as a function of the thickness (*d*) of film grown Sn solution of the melt at different temperatures T_{SC} and T_{EC}

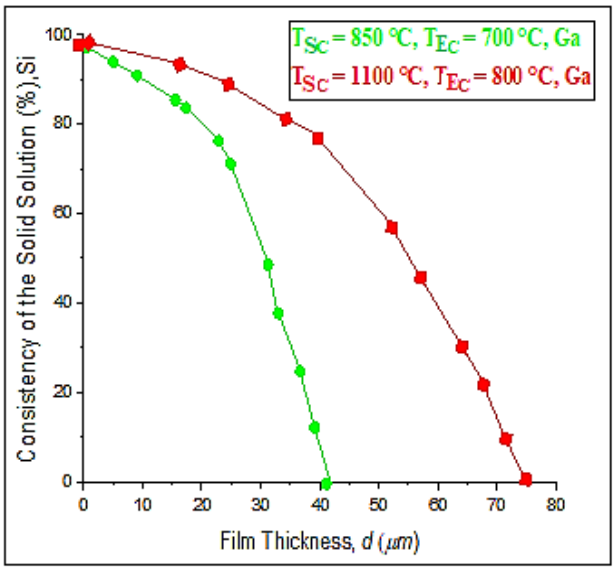

Figure 5: The Si_{1}-$_{x}Ge_{x}$ solid solution composition as a function of the thickness (*d*) of film grown Ga solution of the melt at different temperatures T_{SC} and T_{EC}

In our graded-gap $Si_{1-x}Ge_x$ solid solution, the composition of the films changed in thickness, so we can consider $d_i = f(x)$ (see Figures 3,4). Then, as a complex function, the dependency of dislocations *Ni* on composition x takes the following form: $N_i = ae^{bf(x)}$.

For a specific $Si_{1-x}Ge_x$ sample, in this case, the semi-empirical formula is expressed as:

$N_i = 113213e^{-0.092(-0.0721\,x^2 - 0.0875\,x + 101.09)}$.

With an accuracy of 9.8%, this calculation can determine how much the composition affects the dislocation density.

Following these tests, it was determined that the solid solution component content depends on the film thickness and this was known as the function $di = f(x)$. The experiment revealed that, while the formula is nearly linear for film thickness (d) less than 20 μm, it exhibits a quadratic dependence as d increases beyond 20 μm. This demonstrates that as the T_{SC} of the solid solution increases due to silicon and germanium being highly soluble in the solvent at the start of growth, the silicon content moves slowly in the direction of growth. In contrast the germanium content gradually increases until it reaches the lowest T_{SC}. Through growth, single-crystal Si(111) was used as substrates. Because the composite of the $Si_{1-x}Ge_x$ stable solid solution modifies along the growth direction and is graded-gap, growth is carried out from a partially melted solution (here, the gap between the substrates, in which the melted solution was located, was left unchanged at δ= 1 mm).

The Vegard law, which can be represented as a first approximation of a linear relation, states that the value of the crystal lattice constant of the semiconductor solid solution $Si_{1-x}Ge_x$ (where a_{Si1-x} , a_{Si}, and a_{Ge} were the solid solution's lattice parameters, Si and Ge) can vary smoothly into a specific range of values according to the composite:

$$a_{Si_{1-x}\,Ge_x} = a_{Ge} - xa_{Ge} + xa_{si} \ .$$

Due to this, we can avoid a sharp discrepancy between the lattice parameter on the "substrate-film" structure while the epilayers on the substrate are growing.

On a silicon substrate, observations and semi-empirical mathematical computations have demonstrated the dominant factor at T_{SC}.

With an increase in T_{SC}, the solid solution's epitaxial layer contains an increase in dislocation density. The graph shows that the slope at different T_{SC} is nearly the same, indicating that N_d has a regular dependence on T_{SC}.

Conclusions

The experiments were carried out in a variety of solvents to decrease T_{SC}. The best regime by lesser dislocation (9×10^4–10^5 cm^{-2}), which satisfies the requirements of instrumentation, was obtained at the "substrate– film" interface in the T_{SC} mode = 950 °C from tin, in the T_{SC} mode = 850 °C from gallium melt solutions on a silicon substrate by <111> orientation. Forced cooling was applied in the 0.5 mm to 1.5 mm gap between the substrates. These experimental data can be used to obtain $Si_{1-x}Ge_x$ solid solutions on a silicon substrate with the lowest densities and dislocations with given electro-physical parameters in manufacturing of devices based on them.

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