

Investigation on solid phase epitaxy of deposited SiGe film on a Si substrate

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Abstract

The solid phase hetero-epitaxy of amorphous SiGe on a Si(100) substrate has been investigated. The initial SiGe was deposited by ion beam sputtering at room temperature from a composite target of Si and Ge wafers. The solid phase epitaxial SiGe layer was formed through a boron diffusion, thermal annealing and oxidation process, respectively. The boron diffusion was carried out at 970 °C and then 1065 °C for redistribution, thermal annealing was carried out at 1000 °C in a N₂ ambient, and oxidation at 900 °C in steam, dry O₂ and steam ambient subsequently. Auger electron spectroscopy, X-ray diffraction, scanning electron microscopy, Rutherford backscattering spectroscopy/channeling, cross-sectional transmission electron microscopy, and Raman Spectroscopy were used to characterize the SiGe film. The experimental results indicate that through a boron diffusion, Ge atoms diffuse considerably generating a SiGe layer with a lower Ge concentration than that of the as-deposited film, while the thermal annealing makes the amorphous SiGe layer crystallize, for the oxidation of the a-SiGe/Si structure, a newly formed SiGe/Si heterostructure with a higher Ge concentration than that of the as-deposited film has been found due to the selective oxidation of Si at the applied temperature. © 1997 Elsevier Science S.A.

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1. Introduction

SiGe film has been considered to be a new prospective material for microelectronics. Its applications in heterojunction bipolar transistors (HBTs), modulation doped field effect transistors (MODFETs), and thin film transistors (TFTs), etc., have shown great prospects [1–3]. There is intensive research work regarding SiGe devices and materials. The SiGe/Si heterostructure can be grown by molecular beam epitaxy (MBE) or ultra high vacuum chemical vapor deposition (UHV-CVD). However, there are also efforts to develop other techniques more compatible with Si technology. Solid phase epitaxy (SPE) has attracted much interest recently.

The homogeneous SPE process had been investigated since the 1970s. Lau et al. reviewed the SPE process in Ref. [4]. The kinetics of SPE were also studied in Ref. [5]. Recently, the solid phase hetero-epitaxy of SiGe on a Si

substrate has been reported. Hong et al. demonstrated the SPE SiGe on Si(111) through a Pd₂Si layer [6]. Mohajerzadeh et al. reported a low-temperature ion-beam assisted deposition method realizing SiGe/Si heterostructures with good rectifying behaviour [7]. The Ge implantation into the Si substrate to form a SiGe layer [8–10] and its device applications [11,12] have been investigated. And the SPE SiGe by wet oxidation has been reported by Prokes and Rai [13–15]. Also, the SPE via Ge_xSi_{1-x}O₂ reduction can be found in the literature [16,17]. There is research work focused on the SPE mechanism of SiGe [18,19]. To reduce the mismatch of SiGe with Si, research on incorporation of C into SiGe to form a SiGeC ternary compound matched with Si has made progress [20,21].

In this work, the SPE growth of an ion beam sputtered SiGe film on a Si(100) substrate has been investigated. Some interesting results have been obtained. The SiGe film was deposited from a composite target of Si and Ge wafers at room temperature. Through a boron diffusion at 970 °C and 1065 °C redistribution in N₂ ambient, Ge atoms diffuse significantly, forming a SiGe layer with a lower Ge concentra-

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tion than that of the as-deposited film, the annealing of the amorphous SiGe at 1000 °C makes this layer crystallize, and after an oxidation of a-SiGe/Si at 900 °C, a new SiGe layer with a higher Ge concentration than that of the as-deposited film is formed due to the selective oxidation effect. The processes applied in this study are conventional Si technology and will have good compatibility with the integrated circuit fabrication foundry.

2. Experiments

A $\text{Si}_{0.5}\text{Ge}_{0.5}$ layer was deposited by ion beam sputtering on a Si(100) substrate which has a resistivity of 7–12 $\Omega\text{ cm}$. Si wafers were RCA cleaned, dipped in a buffered HF solution and rinsed in de-ionized water before loading into the Oxford sputtering chamber with a base pressure of 10^{-7} Torr. SiGe film was then sputtered from a composite target of Si and Ge wafers under an Ar pressure of $(6-8) \times 10^{-5}$ Torr with a rate of $0.8 \text{ \AA s}^{-1}$. The SPE was achieved by thermal processes such as a boron diffusion, annealing and oxidation. The boron diffusion was carried out at 970 °C for 20 min, followed by a redistribution at 1065 °C for 10 min in a N_2 ambient. The furnace annealing was carried out at 1000 °C for 10 min in a N_2 ambient. The oxidation was carried out at 900 °C for 10 min in a dry O_2 ambient, then 60 min in a steam ambient, and finally 10 min in a dry O_2 ambient. Auger electron spectroscopy (AES), X-ray diffraction (XRD), scanning electron microscopy (SEM), Rutherford backscattering spectroscopy/channelling (RBS/C), cross-sectional transmission electron microscopy (XTEM), and Raman spectroscopy were used to characterize the film.

3. Results and discussions

3.1. SPE growth of SiGe through boron diffusion

Fig. 1 gives the AES depth profiles of the sputtered SiGe layer after the boron diffusion. Because of the reaction during the boron diffusion: $\text{B}_2\text{O}_3 + \text{Si} \rightarrow \text{SiO}_2 + \text{B}$, there is oxidation accompanying the boron diffusion. Since the heat of formation of SiO_2 ($-200 \text{ Kcal mol}^{-1}$) is much higher than that

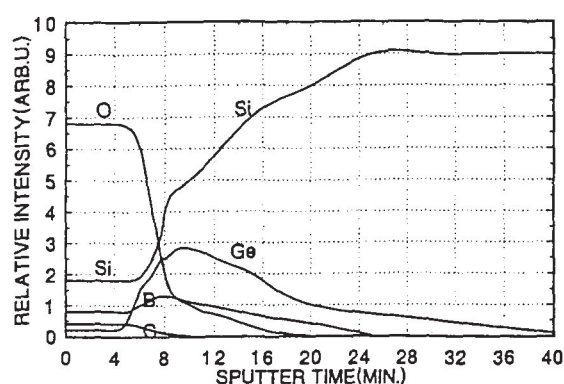


Fig. 1. AES depth profiles of the deposited SiGe/Si sample after the boron diffusion.

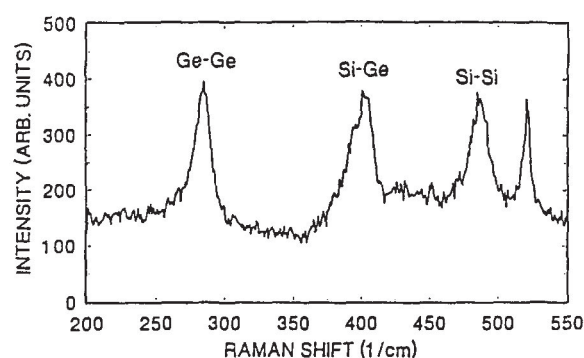


Fig. 2. Raman spectra of the deposited SiGe/Si sample after the boron diffusion.

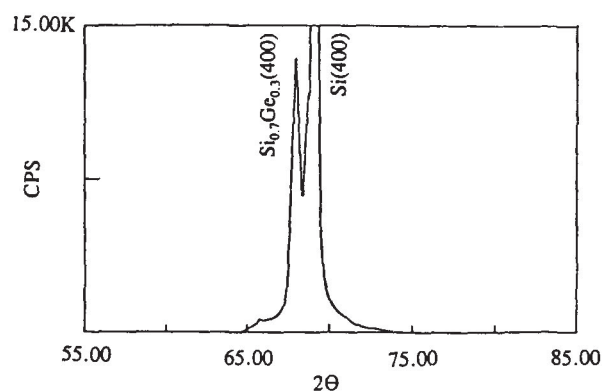


Fig. 3. XRD patterns of the deposited SiGe/Si sample after the boron diffusion.

of GeO_2 ($-130 \text{ Kcal mol}^{-1}$), the selective oxidation of Si takes place [22]. With the formation of SiO_2 on top, the pile-up of the rejected Ge and the segregation of boron atoms towards the SiO_2 layer can also be seen. The Raman measurement was carried out at room temperature with a 488 nm Ar laser. Fig. 2 is the Raman spectra of the sample. The vibration peaks at 286 cm^{-1} , 405 cm^{-1} , and 487 cm^{-1} are associated with the pairs of Ge-Ge, Si-Ge and Si-Si from the SiGe layer, respectively. The measured Raman spectra are very similar with those from MBE-grown sample [23]. Shown in Fig. 3 is the XRD spectra which gives the phase identification of the SiGe layer. Close to the substrate Si(400) diffraction peak, the peak at $2\theta = 68.04^\circ$ with an interplanar distance of $1.376 \text{ \AA}$ should be related to the SPE-grown SiGe layer, and its overall composition can be calculated to be $\text{Si}_{0.7}\text{Ge}_{0.3}$. Fig. 4(a) displays the XTEM micrograph of the boron-diffused SiGe/Si sample. Although there are threading dislocations and stacking faults, a flat interface can be seen. According to the AES depth profiles (Fig. 1) and energy dispersive spectrometry (EDS), the layer structure can be given in the inset of Fig. 4(a). It indicates that the top layer has an average composition of $\text{Si}_{0.4}\text{Ge}_{0.6}$, while below the interface the SiGe layer has a lower Ge concentration than that of the top layer. The overall composition will be $\text{Si}_{0.7}\text{Ge}_{0.3}$ as measured by XRD measurement. Fig. 4(b) is the selected area diffraction patterns taken across the SiGe interface, it shows a good alignment of diffraction spots due to the top $\text{Si}_{0.4}\text{Ge}_{0.6}$ layer and the bottom SiGe layer, and also

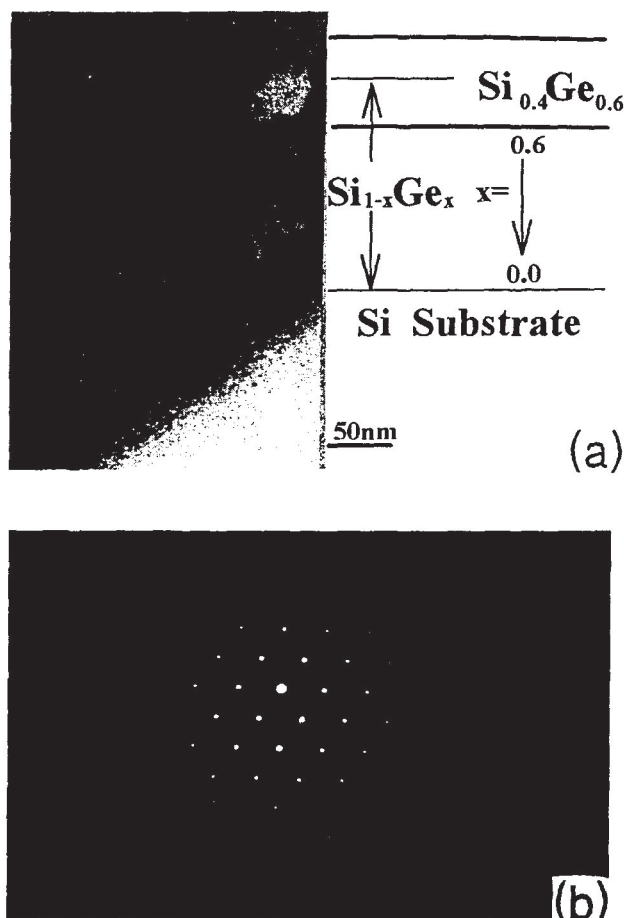


Fig. 4. (a) XTEM micrograph of the deposited SiGe/Si sample after the boron diffusion and (b) the selected area diffraction patterns taken across the SiGe interface.

it indicates a single-crystalline SiGe structure. The SEM micrographs show that the sample has a smooth surface.

The experimental results reveal that the SPE growth of SiGe during the boron diffusion is accompanied by Ge diffusion from the as-deposited SiGe layer. The substitutional Ge diffusion may be enhanced by the boron diffusion. The AES and XRD results show the graded and lower Ge concentration in the SPE SiGe layer than the as-deposited layer. The XTEM micrograph clearly gives the evidence of the Ge diffusion. The interface shown in the XTEM micrograph should be the initial interface of the a-SiGe/Si structure when deposited at room temperature. With the Ge atoms diffusing inward, a lower Ge-content SiGe layer than that of the as-deposited is formed under the initial interface. Since the diffusion is occurring, the interface for the SPE SiGe with a Si substrate is not clear, but the defects show the difference of this layer from the substrate. It is also interesting to note that the SiGe layers across the initial interface have a good alignment.

3.2. SPE growth of SiGe by thermal annealing

Fig. 5 gives the XRD patterns of the SiGe/Si heterostructure after the 1000 °C, 10 min anneal. The diffraction peak at

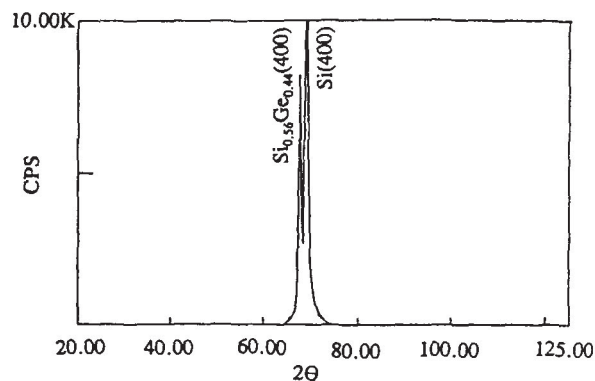


Fig. 5. XRD patterns of the deposited SiGe/Si sample after the thermal annealing at 1000 °C for 10 min.

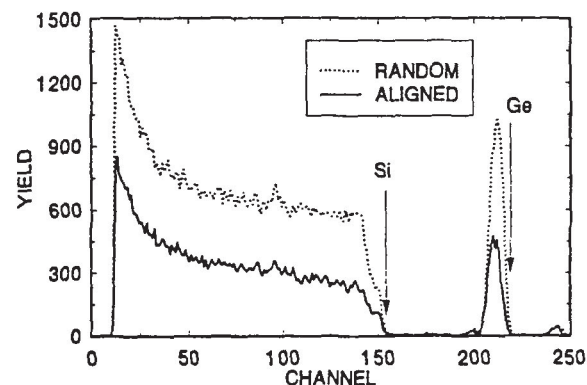


Fig. 6. RBS/C spectra of the deposited SiGe/Si sample after the thermal annealing at 1000 °C for 10 min.

$2\theta = 67.74^\circ$ with $d = 1.382 \text{ \AA}$ is related to the SPE SiGe film, and this film has a similar composition to the as-sputtered layer, $\text{Si}_{0.56}\text{Ge}_{0.44}$. No SiGe peaks from other orientations are detected, indicating the epitaxial character of this crystallized film. Fig. 6 is the RBS/C spectra of the SPE SiGe layer, a significant channelling effect for the SPE SiGe layer can be seen. These results indicate that by thermal annealing, an amorphous SiGe layer on Si substrate may crystallize uniformly without composition changing.

The SPE growth of SiGe by thermal annealing involves the direct transition from amorphous to crystalline structure. The thermal annealing does not generate considerable Ge diffusion, leaving the nucleation process as the dominate factor. This process has some similarities with the previously reported homogeneous SPE growth of Ge [24]. The mismatch and strain in the hetero-epitaxy structure will need further investigation.

3.3. SPE growth of SiGe by thermal oxidation

The oxidation behavior of SiGe has been studied by several groups [25–27], and some interesting phenomena have been found, such as the selective oxidation at high temperatures, the SPE growth during wet oxidation etc. [13–15].

Fig. 7 gives the RBS spectra of the SiGe/Si sample before and after the 900 °C oxidation. The surface SiO_2 formation and the inward migration of Ge can be clearly seen. With the

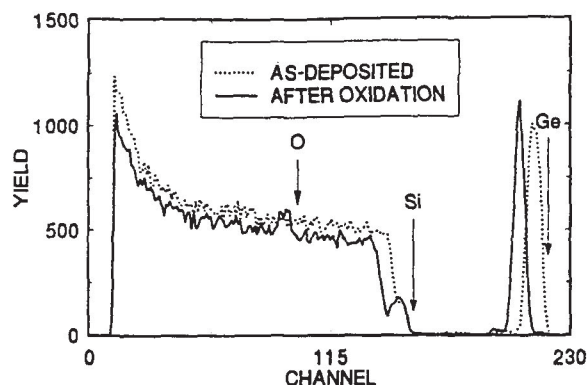


Fig. 7. RBS spectra of the deposited SiGe/Si sample before and after the thermal oxidation.

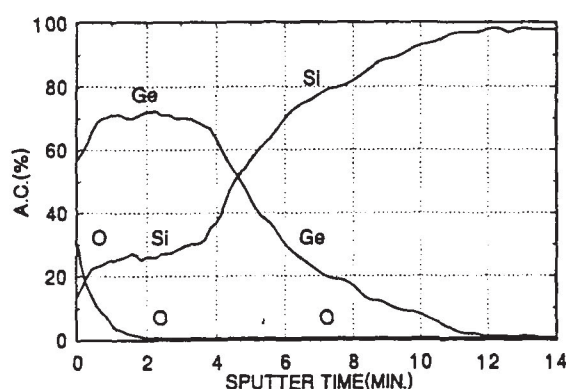


Fig. 8. AES depth profiles of the deposited SiGe/Si sample after the thermal oxidation and the surface SiO₂ removal.

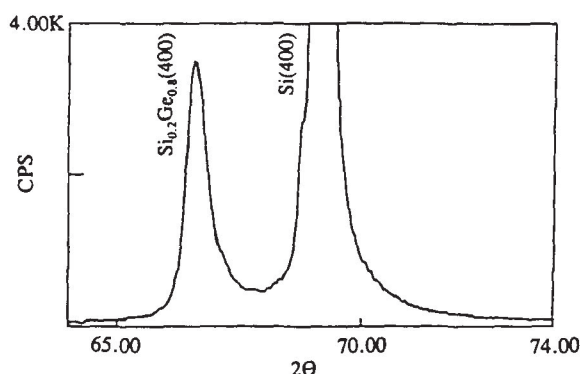


Fig. 9. XRD patterns of the deposited SiGe/Si sample after the thermal oxidation.

Ge peak becoming narrower, a redistributed SiGe layer has been formed. Consistent with the RBS spectra, the AES depth profiles after the surface SiO₂ removal (Fig. 8) show a uniform Si_{0.2}Ge_{0.8} Ge-rich layer. The XRD patterns in Fig. 9 identify the Si_{0.2}Ge_{0.8} layer formation along the Si(100) substrate orientation, indicating the SPE character. Fig. 10 is the RBS/C spectra of the sample, showing that the SiGe film exhibits a significant channelling effect.

According to the model of Prokes and Rai [14], the SPE growth during oxidation lies in the atomic replacement during the selective oxidation of Si. But this mechanism did not explain the Ge-rich SiGe formation which has also been

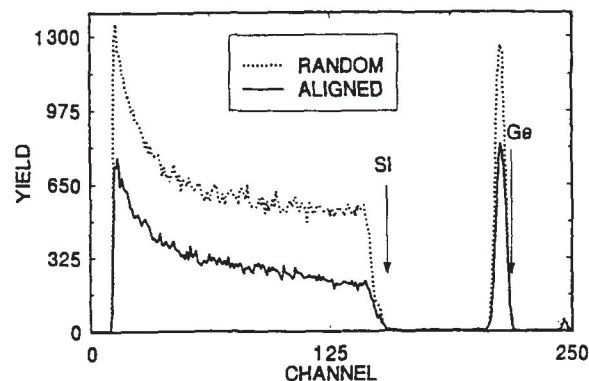


Fig. 10. RBS/C spectra of the deposited SiGe/Si sample after the thermal oxidation and the surface SiO₂ removal.

found by others [6]. The SPE growth during oxidation must have some relations with the nucleation of the rejected Ge atoms. When the SiGe/Si structure is oxidized, the selective oxidation effect makes the Si atoms move to the surface region forming an oxide, and Ge atoms are rejected, forming a Ge-rich layer beneath the surface SiO₂ which may serve as a barrier layer for the Si out-diffusion. When the balance between the Si atoms being oxidized and those diffusing through the Ge-rich layer has been reached, this Ge-rich layer will have a stable composition. Consequently, the nucleated layer will be Ge-rich in composition and exhibit an epitaxial character on Si substrate.

4. Conclusions

The SPE growth of an ion beam sputtered SiGe film on a Si(100) substrate has been studied. The results reveal that SPE SiGe with different compositions and growth mechanisms can be achieved by thermal processes such as diffusion, annealing and oxidation. The boron diffusion enhances the Ge diffusion and a SiGe layer with a lower Ge concentration than that of the as-deposited has been formed. The annealing of the a-SiGe makes the SiGe film crystallize. Through the oxidation of the a-SiGe/Si, a new SiGe layer beneath the surface SiO₂ with a higher Ge concentration than that of the as-deposited is formed due to the selective oxidation of Si at the applied temperature.

It should be noted that the SPE SiGe layer has many dislocations and defects which will have some restriction for its device applications. However, work on the solid phase epitaxy together with the dopant activation [28,29] have shown that it is possible to reduce the defect density while achieving a better dopant activation. How to improve the quality of the SPE layer and investigate the electrical properties of this SiGe/Si structure are now being carried out.

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