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# X-ray-reflectivity study of Ge-Si-Ge films

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Here we report on an x-ray specular reflectivity study of Ge-Si-Ge trilayers grown on Si(001) single-crystal substrate by ion beam sputtering deposition at various substrate temperatures. The electron-density profile of the trilayer as a function of depth, obtained from x-ray-reflectivity data, reveals an intermixing of Si and Ge. The x-ray-reflectivity data have been analyzed using a scheme based on the distorted-wave Born approximation, and the validity of the analysis scheme was checked using simulated data. Analyzed results provided information regarding interdiffusion in this system. We notice that although the Si-on-Ge interface is sharp, a $Si_{0.4}Ge_{0.6}$ alloy is formed at the Ge-on-Si interface. [S0163-1829(96)01947-9]

## I. INTRODUCTION

Silicon-germanium multilayered structures are being studied actively for their possible device applications.[1] The device performance strongly depends on the quality of the different layers in multilayers, and that in turn depends on the growth process.[2] Characterizing the chemical profile of a multilayer film across the depth with angstròm resolution is of immense technological importance. Various techniques are available to characterize the depth profile of the film, such as, secondary-ion-mass spectroscopy, Auger electron spectroscopy, and x-ray photoemission spectroscopy. Most of these techniques are destructive, and have various unwanted effects such as preferential removal rates, intermixing and alloying during the analysis process. Grazing incidence x-ray reflectivity (GIXR) is a nondestructive technique which can give information about the chemical profile across the depth of the film without any unwanted effects during the data collection. GIXR yields information[3–5] about layer thicknesses, surface and interfacial roughnesses and, in general, the electron-density profile (EDP) as a function of depth $z$, taken to be zero at the top of the film, and this technique has been applied recently in Si-Ge systems.[6,7] In GIXR measurements, the intensity of the scattered x ray is measured from a sample surface, keeping the incident and scattered angles equal. The specular x-ray reflectivity data as a function of the vertical component of the momentum transfer $q_z$ $[=2k=(4\pi/\lambda)\sin\theta$, where $\theta$ is the incident angle and $\lambda$ is the x-ray wavelength], is obtained from this measurement by subtracting the diffuse background x-ray intensity. Though the experiment seems to be straightforward, and can yield the EDP of the film, analysis of the reflectivity data still remains a difficult task.

In this paper we present results of a GIXR study of Ge-Si-Ge trilayer grown on a Si(001) single-crystal substrate using the ion-beam sputtering deposition (IBSD) technique. We analyzed the x-ray reflectivity data using the distorted-wave Born approximation technique, and extracted the EDP of a multilayer film without assuming *a priori* distribution. We can determine the chemical composition of the Ge-Si-Ge film from this EDP, and obtain interesting information regarding interdiffusion in Si-Ge interfaces.

The data could be analyzed using this scheme because it was observed that the diffuse scattering[4] intensity in these samples is negligible. We also confirmed by taking diffraction data that the samples are not epitaxial. This indicates that the in-plane correlation length[4] is very small, and simultaneous analysis[6–9] of specular and diffuse data is not required. As a result we assumed that a series of slices, which represent laterally averaged refractive-index depth profile, can be used to analyze the background subtracted reflectivity data.[10] To test this method of GIXR data analysis, we carried out a simulation study for a model Ge-Si-Ge trilayer on a Si substrate that is similar to our samples.

## II. EXPERIMENTAL DETAILS

The Si(001) single-crystal substrates were cleaned by vapor degreasing, then dipped in 10% HF to remove the native oxide, and subsequently rinsed in flowing deionized water. The substrates were then loaded in the vacuum chamber with a target to substrate distance of 8 cm. The IBSD system employs a Kauffman-type ion source of 3-cm diameter. The Ar-ion beam with an energy of 1 keV and a current of 3-mA intensity is incident on the target at an angle of 50° to the target surface normal. During the sputtering the pressure in the chamber was maintained at $3\times10^{-5}$ torr. Films were deposited onto the substrates maintained at 100 ° (sample 1) and 400 °C (sample 2), with a rate of deposition of 0.3 and 0.26 Å/s for Si and Ge, respectively. The nominal thickness of the Si layer was estimated to be about 35±3 Å, and for Ge 35±4 Å. GIXR measurements were performed using a high-resolution diffractometer (OPTIX MICROCONTROLE) with Cu $K_{\alpha,1}$ x rays obtained from a 18-kW rotating anode (Enraf Nonius FR591) x-ray generator and Si(111) monochromator.

## III. SIMULATION

We now present a brief description of the analysis technique, and demonstrate its utility in Ge-Si-Ge systems using

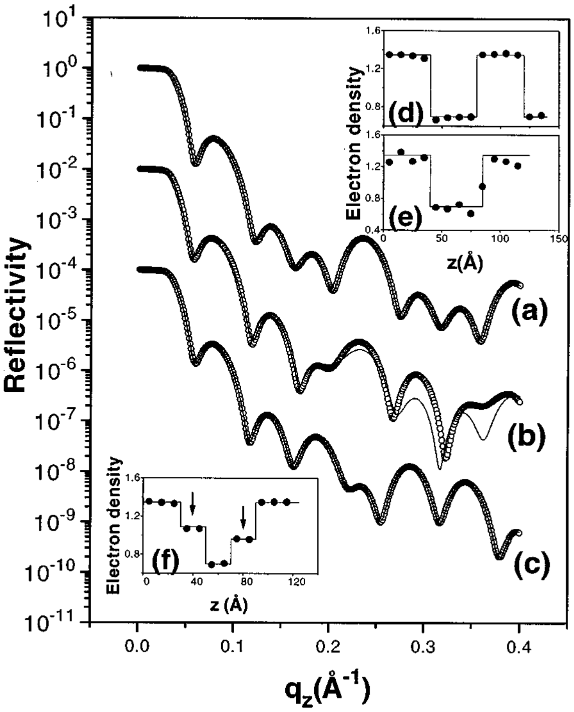

FIG. 1. (a)–(-c) X-ray reflectivity for the model systems (described in the text) [○, simulated data; solid line, fit]; (d)–(f) Electron density profile (EDP) of the model (solid line) and that obtained from the fit (●) for the three model systems studied. In this and other two figures, reflectivity profile have been shifted vertically for clarity.

simulated data. Following Ref. 3, where the film was considered to be composed of a number of thin slices or boxes of electron density $\rho_i$, the reflectivity of the film using the distorted-wave Born approximation is given as

$$R(k)=\left|ir_0(k)+\frac{(2\pi b)}{k}\left(a^2(k)\Delta\rho(q_z^f)+b^2(k)\Delta\rho^{\star}(q_z^f)\right)\right|^2, \tag{1}$$

where $r_0(k)$ is the specular reflectance coefficient of the film with an average electron density (AED) $\rho_0$, and $\Delta\rho(q_z^f)$ can be written[3,4,11] in terms of $\Delta\rho_i$ (=$\rho_i$ - $\rho_0$) of thickness $d$ of the $i$th box as

$$\Delta\rho(q_z^f)=\frac{i}{q_z^f}\left[\left(\sum_{j=2}^{j=N}(\Delta\rho_j-\Delta\rho_{j-1})\exp(iq_z^f(j-1)d)\right)+\Delta\rho_1-\Delta\rho_N\exp(iq_z^fNd)\right], \tag{2}$$

where $N$ is the total number of boxes used in the calculation. Other parameters are defined in Refs. 3 and 11. By selecting an appropriate number of slices and $\rho_0$ of the film, we fit Eq. (1) with $\Delta\rho_i$ as the fit parameters after convoluting the data with a Gaussian instrumental resolution function.

To test this analysis scheme, we simulated the data by generating a reflectivity curve for a Ge/Si/Ge trilayer having a thickness of 40 Å each on a silicon substrate using Parrat's formalism[12] [open circles in Fig. 1(a)]. The AED's of Ge and Si were taken to be 1.35 and 0.7 $\mathrm{Å}^{-3}$ respectively. The present scheme was used to fit the generated curve to obtain back this trilayer EDP. For fitting the generated reflectivity curve we decided to choose 14 slices of 10 Å each, thus overestimating the total thickness of the film. The AED ($\rho_0$) of the film was taken to be 1.133 $\mathrm{Å}^{-3}$. No *a priori* distribution was assumed in EDP, and the starting estimates of all $\Delta\rho_i$'s were taken to be zero. In Fig. 1(d) we show the obtained EDP of the film from the present scheme. This EDP matches well with the original profile, but we notice a small fluctuation around the original value. We also observe that our overestimation of the film thickness led to a determination of the EDP of the substrate at the proper place. The generated reflectivity curve using Parrat's formalism with the original EDP and the obtained EDP from the present scheme is found to be identical [refer to Fig. 1(a)].

Next we studied the effect of the interface lying within a box. By assuming Ge/Si/Ge has thicknesses 40/45/35 Å, and by keeping the box sizes at 10 Å, the interface of Si/Ge is forced inside the ninth box. The reflectivity curve for the above profile is shown in Fig. 1(b). The EDP obtained using the present scheme is shown in Fig. 1(e). We observe that the AED of the ninth box at z=90 Å is the weighted electron density of Si and Ge [(1.35 + 0.7)/2]. The reflectivity curve generated using the obtained EDP is considerably different [the solid line in Fig. 1(b)] from the original reflectivity curve [open circles in Fig. 1(b)]. The fit cannot be improved unless the box size is reduced to represent the EDP properly.

We also tried to see whether the intermixing of layers can be detected using this scheme. We took a model system Ge/$\mathrm{Ge}_{0.6}\mathrm{Si}_{0.4}$/Si/$\mathrm{Ge}_{0.4}\mathrm{Si}_{0.6}$/Ge with layer thicknesses of 30/20/20/20/30 Å each. In Fig. 1(f) we show the obtained EDP and the generated reflectivity curve from the original EDP, and the obtained EDP in Fig. 1(c). The EDP marked by arrows in Fig. 1(f) indicates the intermixing of Si/Ge ($\mathrm{Ge}_{0.6}\mathrm{Si}_{0.4}$ and $\mathrm{Ge}_{0.4}\mathrm{Si}_{0.6}$). The above simulation studies reveal that one can obtain the chemical composition of the film across its depth from x-ray specular reflectivity data if the proper size of the box is chosen. We now use the above method to analyze the specular reflectivity data of IBSD Ge/Si/Ge trilayers on the Si(001) substrate described earlier.

## IV. EXPERIMENTAL RESULTS AND DISCUSSION

In Figs. 2(a) and 2(b) we show the x-ray reflectivity data of Ge/Si/Ge trilayers deposited at 100 °C (sample 1) and at 400 °C (sample 2), respectively. The period of oscillations in the reflectivity curve characterizes the thickness of the layers. The amplitude of the oscillations depends on the contrast of the AED's at the interfaces. From Fig. 2 we see that the period of oscillations of the reflectivity curve for sample 1 is greater than that of sample 2, indicating that the layer thickness of sample 1 is less than that of sample 2. We also observe that the amplitude of oscillations of the reflectivity curve for sample 1 is larger than that of sample 2, which shows that the contrast in AED's at the interfaces for sample 1 is larger than sample 2. To quantify the above observations, we use the method of analysis of the x-ray specular reflectivity data discussed above. To fit the reflectivity curve of sample 1 we used 25 boxes of 8 Å each to model the trilayer film. The best fit of the reflectivity curve was obtained using $\rho_0$ of the film to be 0.85 $\mathrm{Å}^{-3}$ (for an ideal case

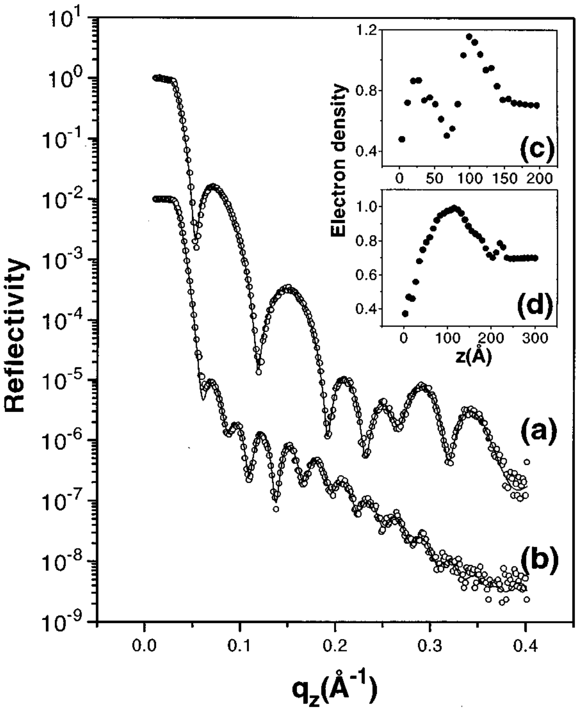

FIG. 2. (a) and (b) X-ray reflectivity for a Ge/Si/Ge trilayer deposited with a substrate temperature of 100 °C (sample 1) and 400 °C (sample 2), respectively [○, data; solid line, fit]; (c) and (d) EDP obtained from the fit to the above data for 100 °C (sample 1) and 400 °C (sample 2), respectively.

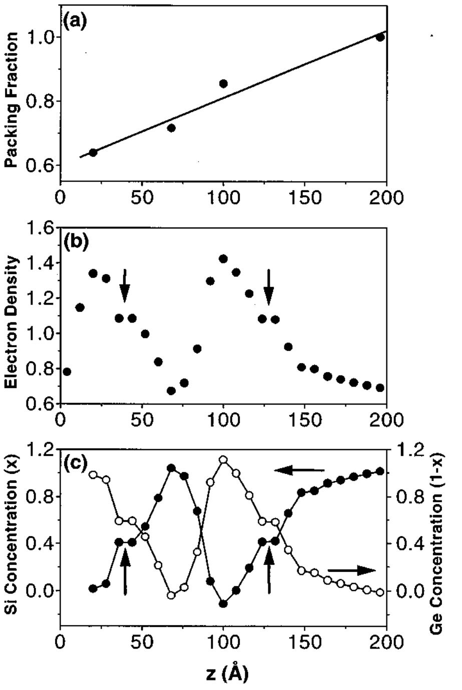

FIG. 3. (a) Packing fraction as a function of depth for sample 1 (solid line: linear fit). (b) Normalized electron density as a function of depth for sample 1. (c) Concentration of Si (●) and Ge (○) as a function of depth for sample 1 (refer to the text for details).

the value of $\rho_0$ for the trilayer should be 1.13 $Å^{-3}$; the significance of $\rho_0=0.85$ $Å^{-3}$ is discussed below). The absorption coefficient $\mu$ for the film was also found to be low $\sim 1.73\times 10^{-6}$ $Å^{-1}$ for the best fit ($\mu$ for bulk Si is $1.43\times 10^{-6}$ $Å^{-1}$, and for bulk Ge is $3.38\times 10^{-6}$ $Å^{-1}$; hence for an ideal film the averaged $\mu$ should be around $2.73\times 10^{-6}$ $Å^{-1}$).

The obtained EDP of sample 1 is shown in Fig. 2(c). Since the thickness of the film was overestimated, we detect the substrate starting from 150 Å. The EDP clearly shows three distinct regions: the two-electron-density maxima for the Ge layers, and a minimum due to the Si layer between the two Ge layers. The obtained electron densities of Ge and Si of the film are found to be low. We also see a lowering of the electron density at the surface due to surface roughness. With this EDP we generated the reflectivity curve using Parrat's formalism. We show this in Fig. 2(a) (solid line) along with the experimental data (open circles).

Similarly, for sample 2 we divided the film into 38 boxes of 8 Å each. The best fit of the reflectivity curve was obtained taking $\rho_0$ of the film to be 0.80 $Å^{-3}$ and $\mu$ $\sim 1.73\times 10^{-6}$ $Å^{-1}$, the same as in sample 1. The obtained EDP is shown in Fig. 2(d). The substrate starts from 200 Å, and we also observe that a strong intermixing has occurred. The first layer of Ge has diffused into the substrate and into the middle Si layer, modifying the EDP of the film as shown in Fig. 2(c). In earlier works,[13–16] it was observed that Ge segregation occurs on Si(001) surface during molecular-beam epitaxial (MBE) growth. This segregation increased to a maximum at around 450 °C, and decreased above this temperature. Using hydrogen as a surfactant supresses Ge segregation at the Si/Ge(001) interface.[16] Ge segregation is observed even in $Ge_{1-x}Si_x$/Si interfaces grown by MBE,[17] but it can be supressed by having an adlayer of Ga on the surface of the growing structure.[17] Recently it was demonstrated that an antimony layer deposited on the interface of $Ge_{1-x}Si_x$/Si can also prevent the intermixing of Si and Ge.[18]

The obtained low electron density of the sample may be due to defects, pin holes, voids, or amorphous or poor crystallinity.[2] From the obtained EDP one can estimate the packing fraction of the film as a function of depth. The packing fraction is estimated in sample 1 from the ratio of the electron density at the centers of the Si and Ge regions obtained from the analysis (assuming that at these regions no intermixing has occured) and the electron density of single crystal Si and Ge (without defects), respectively. In Fig. 3(a) we plotted the packing fraction of sample 1 as a function of depth obtained at four regions (the Ge, Si, and Ge regions of the EDP of the layers and the Si substrate). We approximate the variation of the packing fraction as a linear function of depth [refer to Fig. 3(a)]. For amorphous Si (Refs. 19 and 20) and amorphous Ge,[20,21] a density up to 30% lower than the bulk crystalline value has been observed depending on the deposition condition. The reduction of electron-density values found in our analysis is within this limit. By taking the ratio of the obtained EDP with the packing fraction, we obtain an EDP which takes into account the porosity of the film [refer to Fig. 3(b)]. The maximum value of EDP at $\sim 20$ and 100 Å now corresponds to the electron density of the two Ge layers, and the minimum values at $\sim 68$ and 200 Å correspond to the middle layer of Si and the substrate, respectively. In Fig. 3(b), for depth greater than 120 Å, one observes diffusion of Ge into the Si substrate. We observe an interesting feature in EDP at the Ge/Si interfaces. There is a flat region (having a constant electron density) in the EDP at each Ge-on-Si interface (marked by arrows at ∼40 and ∼120 Å), in contrast to a linear variation in the EDP at the Si-on-Ge interface, indicating a sharp interface within the resolution of our measurement. It was observed earlier[22] that, in MBE-grown samples, a Ge-on-Si interface shows higher rms roughness than a Si-on-Ge interface.

We calculated the chemical composition ($x$) across the depth of the film from the EDP values [for $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ with an electron density of $0.7x+1.35$ $(1\text{-}x)$ at each point]. This is shown in Fig. 3(c). From this figure we observe the formation of at least a 16 Å-thick $\mathrm{Si}_{0.4}\mathrm{Ge}_{0.6}$ alloy at the Ge-on-Si interfaces at $z\sim40$ and $\sim120$ Å (marked by arrows). This alloy formation is not observed at the Si-on-Ge interface. It is known[23] that in the growth of heterostructures containing two materials $A$ and $B$, one of the interfaces, for example, $A$ on $B$, can be abrupt whereas the $B$ on $A$ interface can be diffuse. We feel that in the diffuse interface the alloy $\mathrm{Si}_{0.4}\mathrm{Ge}_{0.6}$ has formed. $\mathrm{Si}_{0.4}\mathrm{Ge}_{0.6}$ on a Si substrate grown using MBE has been studied recently.[24] The values of $x$ and 1-$x$ which are greater than 1 and negative are due to the linear approximation of the packing fraction. In the case of sample 2, a strong intermixing of Si and Ge makes it difficult to extract the packing fraction and, as a result, the exact composition across the depth, but one can qualitatively obtain the composition from the EDP shown in Fig. 2(d).

To summarize, we demonstrated that the compositional profile across the depth of a thin film can be obtained by a proper analysis of specular reflectivity data. We illustrated this method using simulated data and measured reflectivity data of Si/Ge/Si trilayers, grown using the IBSD technique. We observed that the intermixing of Si and Ge is low at low temperature, and increases at high temperature. We also observe that although the interface formed by Si over Ge is sharp, a $\mathrm{Si}_{0.4}\mathrm{Ge}_{0.6}$ alloy is formed at the interface when Ge is deposited over the Si layer. Work is now in progress to grow better Si/Ge multilayers using IBSD, and the described x-ray-reflectivity analysis scheme will provide very valuable feedback for the growth process.

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