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Correlation between heterointerface superstructures and alloy composition in Si_xGe_{1-x}/Si heterostructures

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In this paper, we present a simple theory relating the unit-cell size of a heterointerface to the alloy-film composition (x) and we apply it to Si_xGe_{1-x}/Si(111)-7×7 and *a*-Si/$Si_{0.8}Ge_{0.2}$(111)-5×5 heterostructures. The results are analyzed in the light of existing experimental data.

I. INTRODUCTION

While modern growth techniques have now succeeded in bringing to light technological issues in materials science, many aspects of the underlying physics in such growth experiments are under study. The elementary processes involved arise as chemically different atomic species are deposited on a well-characterized substrate surface. A heterointerface structure is then created between two solid-state phases more or less different with respect to their chemical and crystallographic features. It is now a well-established strategy to take advantage of such differences in designing systems showing unusual electronic features. This opens the way to at least two issues: (i) alloying processes which produce an interfacial phase which may be tuned by changing its crystallographic (lattice parameter, two-dimensional unit-cell structure) and electronic (band-gap) features; and (ii) interface strains, induced by lattice-parameter mismatch which may affect the electronic band structure of the system and consequently lead to interesting new behavior.

Investigations of the properties of bare semiconductor surfaces have revealed that the latter show a striking ability to experience a wide variety of surface reconstructions. Although research on interfacial superstructures is still in its infancy, experimental results obtained for some systems show that the interface processes also bring their own plethora of new results. This is to say that interface physics has of course inherited the complexity of surface physics.

The role of strains in surface physics was recognized several years ago, when a model for the Si(111)-7×7 reconstructed surface was proposed.[1] Meanwhile, recent experimental results have paid particular attention to the role of interface strains in heterostructure technology through their involvement in obtaining interface final superstructures and in band-structure shifts. Interface strain mechanisms aim to produce interfaces free of extended defects such as dislocations, provided that the layer thickness is lower than the critical thickness.

In a previous work, we reported[2] on the discovery of a simple correlation between parameters related to the geometry of the superstructure before (substrate surface superstructure) and after (reconstructed buried superstructure) film growth, and the elastic-density properties of materials forming the substrate-deposited film structure. We successfully tested[2,3] this correlation on different heterostructures for which experimental data on interface superstructures exist. For all systems investigated, it has been assumed that interfacial strains play a major role in the stabilization of the final superstructure. These are SiO_2 (coesite)/Si, Ge/Si, $Ge_{0.5}Si_{0.5}$/Si, and *a*-Si/$Ge_{0.2}Si_{0.8}$.

In this paper we concentrate on the Si_xGe_{1-x}/Si system. The latter is of technological interest, and it is expected that it will play an important role in silicon technology. This is because these heterosystems provide a flexible way of designing new devices, as the parameters of the host materials forming the heterojunction can be varied.

The question of the interfacial geometry at the contact of the constituent materials of a heterostructure is a vital one, because of its relevance to interface stability. One may indeed note that such interfacial stability is required in order to produce high-quality interfaces.

This justifies a systematic study, in this system, of interfacial superstructure evolution when x is varied. Doing so, we aim to obtain a diagram showing the evolution of the unit-cell size of the strain-stabilized interface structure as a function of x. In Sec. II, we briefly recall the main features of correlation theory. We then derive an equation which enables us to determine x for a given initial substrate structure and a final buried interface structure. The phase diagram is then calculated, and we compare the results with existing experimental data. To end this section, we must emphasize the usefulness of such a diagram for researches growing from such systems, as it relates the alloying parameter x (of special interest for growth experiments) to the unit-cell size of the interface structure.

II. THE CORRELATION THEORY

Let us now present the basic physics involved in the correlation idea. As in the systems which have been experimentally investigated, a predominant role is assigned to strains in the stabilization of interfacial superstructures. A good starting point for a theoretical approach is to consider the equations of elasticity as, for example, stated for cubic crystals:[4]

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$$\frac{\delta^2 u}{\delta t^2} = \frac{C_{11}\delta e_{xx}}{\rho\delta x} + \frac{C_{12}}{\rho}\left[\frac{\delta e_{yy}}{\delta y} + \frac{\delta e_{zz}}{\delta x}\right] + \frac{C_{44}}{\rho}\left[\frac{\delta e_{xy}}{\delta y} + \frac{\delta e_{zx}}{\delta z}\right] . \qquad (1)$$

In this equation, u is the x component of the displacement, ρ is the density, and the (C_{ij}) and $(e_{\sigma\sigma})$ are, respectively, the elastic constants and the strain components. The equations for the directions y and z can be deduced from Eq. (1). The resulting equations (for x, y, and z) may be considered as the signature of strain-induced processes in lattice dynamics. Consequently, they indeed may be a useful means of identifying the parameters relevant to our approach.

The first important parameter is the ratio (C_{ij}/ρ), which we called the elastic-constant-density factor which links the strain components, via their derivatives, to such dynamic features as $\delta^2 u/\delta t^2$, which is proportional to the square of the angular frequency ω^2. Let us now assume that m and n are the numbers which scale the periodicity of a given superstructure $(m \times n)$. If x and y are the symmetry directions in the interface plane, the two-dimensional structure $(m \times n)$ implies that we must find atoms at each $(m \times a)$ and $(n \times a)$ lattice spacing, respectively, along the x and y directions; here a represents the lattice parameter. The extension of the first two-dimensional Brillouin zone along x and y is respectively equal to $g_x \cong \pi/ma$ and $g_y \cong \pi/na$. The phonon frequency clearly depends on the quantity (C_{ij}/ρ) and $G \equiv 1/g_x g_y \cong (m \times n)a^2$, as $\omega^2 \cong C_{ij}/(\rho G)$. We recognize that ω^2 is the ratio of the elastic-density factor, (C_{ij}/ρ), to the geometric factor G. Let us now assume that the buried interface structure between the substrate and the film is of symmetry $(p \times q)$. One may derive the correlation equation from a phonon-frequency matching relationship between materials A (substrate) and B (deposited film) as

$$C_{11A}/\rho_A G_A = C_{11B}/\rho_B G_B \ , \qquad (2a)$$

and consequently

$$R \equiv S/G = 1 \ , \qquad (2b)$$

where

$$S = S_A/S_B \ , \qquad (2c)$$

$$G = G_A/G_B \ , \qquad (2d)$$

with

$$S_A = C_{11A}/\rho_A \ , \qquad (2e)$$

$$S_B = C_{11B}/\rho_B \ , \qquad (2f)$$

$$G_A \propto (p \times q)a_A^2 \ , \qquad (2g)$$

$$G_B \propto (m \times n)a_B^2 \ . \qquad (2h)$$

We may then relate the feature G_B of the final interfacial structure accommodated by materials A and B, to that, G_A, of the substrate structure through the elastic-density factor S, as

$$G_B = G_A/S \ . \qquad (3)$$

In what follows, we will assume that the substrate (material A) is a Si crystal with a (111)-$m \times n$ surface superstructure. We consider continuous films of $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ (material B) epitaxially grown on this Si(111)-$(m \times n)$ substrate.

III. THE INTERFACE SUPERSTRUCTURE-ALLOY COMPOSITION CORRELATION FOR THE $\mathrm{Si}_x\mathrm{Ge}_{1-x}$/Si HETEROSTRUCTURE

In our theory, a_A, ρ_A, and C_{ijA} represent, respectively, the lattice parameter, the mass density, and the elastic constant associated with the substrate (A) before the creation of the heterointerface. Despite the fact that surface reconstruction may modify a, and that in general the materials parameters may vary near the surface, we assume the bulk approximation.

In the case of a heterostructure, one may consider several situations, depending on the host materials and on the interface structural behavior. If, for example, we consider an AlSb layer epitaxially grown on a GaSb substrate, we deal with a system involving materials with a highly mismatched lattice parameter. As far as the film thickness is smaller than a critical thickness, say h_c, this mismatch may be taken up by interfacial strains, and the in-plane lattice constant of the film layer is equal to that of the substrate. Beyond h_c, the formation of dislocations may be favored from the defect formation energy point of view, and the in-plane lattice parameter of the film may match the substrate parameter.

Let us now analyze the situation for the $\mathrm{Si}_x\mathrm{Ge}_{1-x}$/Si heterostructures. As one knows, Ge and Si are miscible, and alloy solid solutions can be prepared in bulk or by epitaxial growth. If we consider the lattice parameter of Ge-Si alloys, we may assume, as a first approximation, that this parameter obeys Vegard's law with a linear variation between 5.43 Å for Si and 5.63 Å for Ge. Due to this lattice mismatch, the epitaxial growth of these materials does indeed involve large amounts of interfacial strains. Consequently, for a fully coherent strained layer, the epitaxial growth condition implies that we must have identical in-plane lattice constants for the film and the substrate, especially near the interface. However, due to the miscibility of Ge and Si, the actual interface may involve intermixing and the interfacial phases may not be as distinct as are Si and $\mathrm{Si}_x\mathrm{Ge}_{1-x}$/Si. In what follows, we will assume that the in-plane lattice constants a_A and a_B are identical and invariant with respect to the alloy composition:

$$a_B \equiv a_A = a_{\mathrm{Si}} \ . \qquad (4a)$$

The correlation we aim at is, in fact, a relationship involving the relevant parameters S_A, S_B, G_A, G_B, and x, the composition parameter of the germanium-silicon alloy. That parameter is involved through the film parameters, namely ρ_B and C_{11B}, using the relationships

$$\rho_B = (1-x)\rho_{\mathrm{Ge}} + x\rho_{\mathrm{Si}} \ , \qquad (4b)$$

$$C_{11B}=(1-x)C_{11\mathrm{Ge}}+xC_{11\mathrm{Si}} . \tag{4c}$$

Here we assume that the alloy mass density and elastic constant vary linearly with x.

The application of the correlation equation [Eq. (2b)] gives the relationship

$$\frac{(m\times n)a_A^2}{(p\times q)a_B^2}=\frac{C_{11A}}{\rho_A}\Big/\frac{C_{11B}}{\rho_B} . \tag{5}$$

Using Eqs. (4a)–(4c), we derive the following "state-equation:"

$$\frac{p\times q}{m\times n}=\frac{\rho_{\mathrm{Si}}}{C_{11\mathrm{Si}}}\,\frac{(1-x)C_{11\mathrm{Ge}}+xC_{11\mathrm{Si}}}{(1-x)\rho_{\mathrm{Ge}}+x\rho_{\mathrm{Si}}} . \tag{6}$$

Equation (6) gives the interface superstructure $(p\times q)$ which is induced by the epitaxial growth of the $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ alloy on the Si substrate having an $(m\times n)$ surface superstructure. Physically acceptable solutions of Eq. (6) do indeed correspond to $x\in(0,1)$.

We can now obtain the reconstruction diagram of such a heterostructure as a function of the alloy composition x. To do so, we consider that the substrate surface structure is $m\times n=7\times 7$, and we solve Eq. (6) in order to find the interfacial superstructure $(p\times q)$. The following parameters are used.

For crystalline Si,

$$\rho_{\mathrm{Si}}=2.33\ \mathrm{g\,cm^{-3}}\ ,\quad C_{11\mathrm{Si}}=1.66\times 10^{12}\ \mathrm{dyn\,cm^{-2}}\ .$$

For crystalline Ge,

$$\rho_{\mathrm{Ge}}=5.36\ \mathrm{g\,cm^{-3}}\ ,\quad C_{11\mathrm{Ge}}=1.29\times 10^{12}\ \mathrm{dyn\,cm^{-2}}\ .$$

Here, we assume that ρ is equal to its bulk value: we do not take account of the Poisson ratio effect. The results are given in Fig. 1.

First of all, we must check that, for $x=1$, the initial Si superstructure 7×7 is preserved. This is the configuration which must exist as we have now a homointerface between two silicon materials. We do indeed find that $x=1$ is solution of Eq. (6) if we assume that the final interface structure is 7×7.

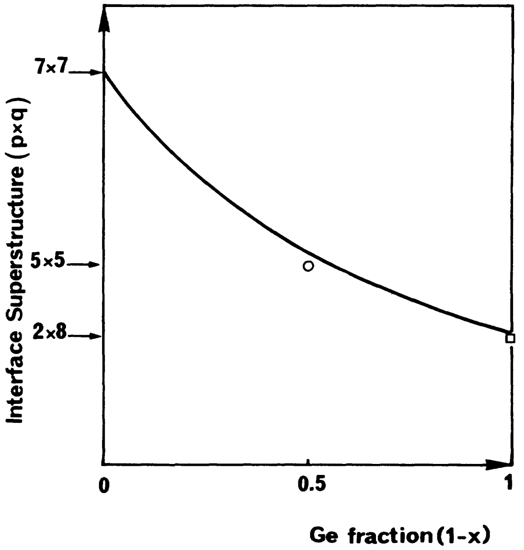

FIG. 1. Evolution of the superstructure of a $\mathrm{Si}_x\mathrm{Ge}_{1-x}$/Si(111)-7×7 heterointerface as a function of the Ge fraction $(1-x)$. Theoretical (solid line) and experimental (□: Ref. 7; ○: Ref. 8) results are shown.

If we consider a pure Ge film grown on a Si(111)-7×7 substrate, the theory predicts a (2×8) interface superstructure (Fig. 1). As it is known, the C (2×8) structure is characteristic of the surface of weakly strained Ge films.[5,6] A correlation between lateral compressive strain and the reconstructed surface structure of a pure Ge film grown on Si(111)-7×7 substrates has been discovered.[7] In the regime of thick overlayers, and when the lateral contraction of the Ge film is decreased, the C (2×8) surface reconstruction of Ge is promoted over the 7×7 structure. If one considers that in the regime of weakly strained films, there exists a symmetry-continuity condition which applies to both sides of the film (one of these being involved in the Ge/Si heterointerface), one may helpfully use Eq. (6) in order to predict the interface reconstruction of the Ge/Si system.

Our results show that when growing a $\mathrm{Ge}_{0.55}\mathrm{Si}_{0.45}$ film on a Si(111)-7×7 substrate, a 5×5 superstructure may stabilize the heterointerface, as it may accommodate the alloy film and the Si lattices. On the other hand, thin films of $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ have been grown by molecular-beam epitaxy (MBE) on Si(111)-7×7 substrates[8] (film thickness ≅65 Å). For $x=0.5$, the low-energy electron-diffraction (LEED) pattern showed a 5×5 surface structure. One may think of a similar interfacial superstructure if a symmetry-continuity condition is applied to both sides of the film. For such low film thicknesses, one may assume that there is a strong interaction between the internal (heterointerface) and external surfaces of the film. In this case, we observe that the theory predicts a fairly reasonable result.

Structural information about solid-solid interfaces may be obtained by synchrotron grazing-incidence x-ray diffraction. The heterointerface structure of an a-Si film grown on a $\mathrm{Ge}_{0.2}\mathrm{Si}_{0.8}$ (111)-5×5 substrate has been monitored by such a technique.[9] It showed that the initial substrate superstructure was preserved after deposition of an amorphous Si overlayer. If we apply the present theory to this heterostructure, we obtain the following equation:

$$\frac{p\times q}{m\times n}=\frac{C_{11a\text{-}\mathrm{Si}}}{\rho_{a\text{-}\mathrm{Si}}}\,\frac{(1-x)\rho_{\mathrm{Ge}}+x\rho_{\mathrm{Si}}}{(1-x)C_{11\mathrm{Ge}}+xC_{11\mathrm{Si}}}\ , \tag{7}$$

where $m\times n$ is now the substrate (alloy) surface superstructure and $p\times q$ the interface superstructure induced by the epitaxial film layer.

Let us recall that the film parameters $C_{11a\text{-}\mathrm{Si}}$ and $\rho_{a\text{-}\mathrm{Si}}$ are calculated by using the following method.

As shown by experimental data on amorphous Si (Refs. 10 and 11), the mass density $\rho_{a\text{-}\mathrm{Si}}$ and Young's modulus $E_{a\text{-}\mathrm{Si}}$ are related to the crystalline state values $(\rho_{c\text{-}\mathrm{Si}},E_{c\text{-}\mathrm{Si}})$ by the following relationships:

$$\rho_{a\text{-}\mathrm{Si}}\cong 0.95\rho_{c\text{-}\mathrm{Si}}\ ,$$

$$E_{a\text{-}\mathrm{Si}}\cong 0.73E_{c\text{-}\mathrm{Si}}\ ,$$

where

$$E_{c\text{-Si}} \cong 1.7 \times 10^{12}\ \text{dyn cm}^{-2}\ .$$

This gives

$$\rho_{a\text{-Si}} \cong 2.21\ \text{g cm}^{-3}\ .$$

The elastic constant $C_{11a\text{-Si}}$ (Ref. 12) may be estimated from the crystalline state value by using the same deficit factor as the one given above (0.73). We then obtain

$$C_{11a\text{-Si}} \cong 1.21 \times 10^{12}\ \text{dyn cm}^{-2}\ .$$

The alloy composition is $x = 0.8$ and the substrate surface structure is $(m \times n) = 5.5$. Equation (7) gives

$$\frac{p \times q}{m \times n} \cong 1\ .$$

This demonstrates that the (5×5) superstructure is a possible candidate for an a-Si/$Ge_{0.2}Si_{0.8}$(111) interfacial superstructure.

Strictly speaking, the a-Si/$Ge_{0.2}Si_{0.8}$(111)-5×5 heterostructure is rather different from the one in which a Si_xGe_{1-x} alloy film is grown on a crystalline Si(111)-7×7 substrate. The analysis of the results presented in this paper shows that, depending on the crystalline quality of the host material, overlayer alloys of different compositions (e.g., $Ge_{0.5}Si_{0.5}$ or $Ge_{0.2}Si_{0.8}$) may lead to the same heterointerface superstructure provided that the growth sequence is inverted.

IV. CONCLUSION

The present analysis of the heterointerface reconstruction processes is based on the role of strains which are induced by the lattice mismatch between the host materials (film and substrate) forming the heterostructure. Within this framework, we develop the idea of the correlation between the superstructure of the heterointerface and the alloy-film composition and we apply the theory to Si_xGe_{1-x}/Si(111)-7×7 heterostructure, as well as a-Si/$Si_{0.8}Ge_{0.2}$(111)-5×5 heterostructures. The trends shown by the derived state equation are in reasonable agreement with existing experimental results.

We hope that this simple approach of the heterointerface reconstruction processes will be useful, as a first approximation, to researchers interested in this field.

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