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Correlation between geometric and elastic parameters in structural modification of interfacial superstructures

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We have discovered that, for systems where strains play a dominant role in interfacial superstructure stabilization, a structural modification of film-substrate interfacial superstructure, subsequent to modern growth conditions, exhibits a strong similarity between geometric and elastic-constant-density factors. An illustration is given for Si/Ge, Si/$Ge_{0.5}Si_{0.5}$, and Si/SiO_2 systems.

The most striking feature of semiconductor surfaces is that they experience a wide variety of surface reconstructions. The actual development of surface technologies enables us to give a reliable evidence for such superstructures, as for example the 7×7 arrangement of Si(111) surface shown by the scanning-tunneling-microscopy technique.[1] The physics involved in modern epitaxial-growth experiments must, of course, deal with the surface problem, as different initial surface arrangements of the substrate may lead to different configurations of the epitaxially grown layers. One vital question here is to find out towards which stable arrangement the initial symmetry of the solid-vacuum surface (substrate) evolves during the growth process. It would then be important to identify also the driving process involved in a possible symmetry modification.

Analyzing the surface reconstruction problems, many authors have recognized the role of strain in taking up the lattice "mismatch" between surface reconstructed layer and the inner part of the crystal. They were then able to suggest, among others, a new model for reconstructed Si(111) 7×7 surface.[2] We are interested here by the interface problem addressed by modern epitaxial growth, where heterojunctions, constituted of materials having different lattice parameters, are elaborated. Recent experimental results have given strong evidence of the role of strains in the stabilization of interface superstructures: For example, when continuous films of pure Ge are epitaxially grown on Si(111) substrates, the surface arrangement switches from the (2×8) symmetry to the well-known 7×7, and it is assumed in this case that this modification is caused by a small compressive strain.[3] It is also supposed[4] that the role of strain is predominant in obtaining the (5×5) superstructure in Si/$Ge_{0.5}Si_{0.5}$. The system Si/SiO_2 has also been studied, and the main issue is that a stable 5×5 reconstruction is induced by application of a tensile strain.

The theory has also concentrated on the relationship between the film thickness and the actual interfacial strain, in order to predict the critical thickness h_c beyond which structural defects should appear, in order to understand the effect of the relative hardness of the materials involved in the growing system. The theory also investigated the influence of interface bond strength on the quality of the device and tried to predict the defect induced symmetry modification. Broadly speaking, these approaches are divided into two types: interfacial energetics-based calculations and atomistic static and dynamic self-consistent calculations.[5-7]

In this paper we report the discovery of a simple correlation between the parameters related to the geometry of the superstructure before (substrate surface superstructure), and after (reconstructed superstructure) film growth and the elastic-density properties of the substrate-film materials. The basic event, which occurs during a reconstruction process, is that under experimental conditions the atoms leave their actual positions towards new stable positions. The initial superstructure $(n\times m)$ associated with the substrate (hkl) surface is transformed into a new one, say $p\times q$. This is a dynamic effect in which the elementary unit mesh $(ma_i\times na_i)$ contracts or extends up to the new one $(pa_i\times qa_i)$ (a_i represents the lattice constant). In such systems where the strains play the main role in this evolution, the parameters entering the elasticity theory of atomic motion are the causal parameters to be considered.[8-10] As for cubic crystals, we recognize this parameter to be the elastic-constant (C_{ij}) -density (ρ) ratio, i.e., the strain coefficient in the equation of motion.

Let us now consider a film made of material A epitaxially grown on a substrate made of material B. We assume that after the growth process the symmetry associated with the unit cell of the substrate free surface $G_B=ma_B\times na_B$ has been modified, leading to a new strain-mediated arrangement characteristic of the film $(G_A=pa_A\times qa_A)$. Our estimation of the film elastic parameters and density is based on the strategy of transfer of the bulk values to the film case. This means that we do not incorporate such effects as the film thickness dependence in the evaluation of C_{ij} because of the lack of this kind of information.

The analysis which we carried out brings us to the conclusion that in such systems, where the reconstruction process is strongly triggered by strain mechanism, there must exist a correlation between the geometric parameters, e.g., the ratio $G=G_B/G_A$ (which is a scale of the relative variation of the unit cell size) and the elastic-density factor, e.g., the ratio $S = S_B/S_A = (C_{ij}/\rho_B)/(C_{ij}/\rho_A)$. We concentrate now on the evaluation of these parameters for some systems in which the role of strains in interfacial rearrangement is well established, that is, in systems in which the elastic waves give the driving forces for overlayer induced deformations. The first one is constituted of pure Ge, grown by molecular-beam epitaxy on Si(111) 7×7 substrates at 550 °C, showing a switch of the 7×7 superstructure to the 2×8 one, related to strained-unstrained films transition.[3] By taking $a_{\mathrm{Si}} \cong 5.43$ Å and $a_{\mathrm{Ge}} \cong 5.65$ Å, and noticing that $m = n = 7$ and $p = 2$, $q = 8$, we obtain $G \cong 2.83$. We come now to the evaluation of the elastic-density ratio S. For Si and Ge we have for Si,

$$C_{11} \cong 1.66\times10^{12}\ \mathrm{dyn\,cm^{-2}} \text{ and } \rho \cong 2.33\ \mathrm{g\,cm^{-3}}\ ;$$

for Ge,

$$C_{11} \cong 1.29\times10^{12}\ \mathrm{dyn\,cm^{-2}} \text{ and } \rho \cong 5.36\ \mathrm{g\,cm^{-3}}\ .$$

This gives $S \cong 2.96$. We then conclude that $R \equiv S/G \cong 0.95 \cong 1$. This result shows a remarkable similarity between the evolution of the geometric and the elastic-density ratios subsequent to the film growth. Let us notice that, rewritten in the following form, i.e.,

$$R \equiv S/G = (S_B/G_B)/(S_A/G_A)\ ,$$

R appears as the ratio of the strain factor strengths, as appearing in the elasticity theory of atomic motion, normalized to the unit mesh sizes. From this point of view the equality $R = 1$ should be understood as a continuity equation near the interface for the normalized strain factor in the epitaxial or the quasiepitaxial growth process.

The next example which we consider concerns $\mathrm{Ge_{0.5}Si_{0.5}}$ alloy films grown by molecular-beam epitaxy on Si(111) substrate.[4,11] This system shows a 5×5 superstructure stabilized by the effect of a compressive strain. In order to calculate the ratios G and S we require the estimation of the relevant alloy parameters, i.e., a, ρ, and C_{11}. The alloy lattice constant a and the density ρ have been measured throughout the entire alloy system.[12] For a $\mathrm{Ge_{0.5}Si_{0.5}}$ alloy we have $a \cong 5.537$ Å and $\rho \cong 3.947$ $\mathrm{g\,cm^{-3}}$.

These values are consistent with the ones calculated by using the relationships

$$a(50\text{ at. \% alloy}) = 0.5(a_{\mathrm{Si}} + a_{\mathrm{Ge}}) \cong 5.544\ \text{Å}\ ,$$

$$\rho(50\text{ at. \% alloy}) = 0.5(\rho_{\mathrm{Si}} + \rho_{\mathrm{Ge}}) \cong 3.85\ \mathrm{g\,cm^{-3}}\ .$$

It turns out that such an average is meaningful, and we extend its application to the alloy elastic constants. We then obtain $C_{11} \cong 1.47\times10^{12}$ dyn $\mathrm{cm^{-2}}$. We now have all the elements required to calculate G (as $m = n = 7$ and $p = q = 5$) and S. We obtain $G \cong 1.89$ and $S \cong 1.91$. This gives $R \equiv S/G \cong 1.01$. We again get a remarkable similarity between the geometric and the elastic-density factors.

The last typical example we now consider is the strained ($\mathrm{Si/SiO_2}$) system,[13] for which it has been shown that a 5×5 reconstruction occurs (here $p = q = 5$). The relevant problem to be sorted out concerns the oxide state near the interface because of the large difference in the parameters values which must be used (a, ρ, c_{ij}). It has been shown[14] that noncrystalline films grow on the silicon substrate with a relatively high degree of short-range order under the silicon substrate influence (quasiepitaxial growth). This means that $\mathrm{SiO_2}$ films are crystalline or present some crystallinelike behavior near the $\mathrm{Si/SiO_2}$ interface as supported by recent x-ray photoemission spectroscopy (XPS), etching, and structural studies. It is then suggested[14] that the initially grown oxide resembles some high-density crystalline polymorph of $\mathrm{SiO_2}$, e.g., coesite structure, although other structures may be involved, e.g., α-quartz structure. We will consider these two possibilities in what follows.

$\mathrm{SiO_2}$: Coesite structure. For this structure we have $a \cong 7.15$ Å; $\rho \cong 2.91\ \mathrm{g\,cm^{-3}}$, while the elastic constant C_{11} can be deduced from the shear modulus and Young's modulus data by using standard relationships (Ref. 15, Table 1). We then obtain $C_{11}(\text{coesite}) \cong 2.16\times10^{12}$ $\mathrm{dyn\,cm^{-2}}$. To be consistent, we may evaluate C_{11} for Si from the same table and by following the same procedure. This gives $C_{11}(\mathrm{Si}) \cong 2.08\times10^{12}\ \mathrm{dyn\,cm^{-2}}$. One notices that this value is higher than the one used for the Si/Ge case. We then obtain $G \cong 1.13$, $S \cong 1.20$, and $R \equiv S/G \cong 1.06$. If on the other hand we use $C_{11}(\text{coesite}) \cong 1.61\times10^{12}\ \mathrm{dyn\,cm^{-2}}$, as determined from Brillouin scattering measurements on a 100-μm crystal,[15] together with $C_{11}(\mathrm{Si}) \cong 1.66\times10^{12}$ dyn $\mathrm{cm^{-2}}$ (see Ref. 16), we find $S \cong 1.29$ and $R \cong 1.14$.

$\mathrm{SiO_2}$: α-quartz structure. For this structure we have $a \cong 4.91$ Å, $\rho \cong 2.65$ g $\mathrm{cm^{-3}}$ and $C_{11} \cong 0.87\times10^{12}$ $\mathrm{dyn\,cm^{-2}}$. Using Si and α-quartz parameters we obtain $G \cong 2.39$, $S \cong 2.20$, and $R \cong 0.92$. Bearing in mind that no adjustment of the parameters has been made, we can notice that the similarity between S and G holds for the $\mathrm{Si/SiO_2}$ system.

Eventually we would like to comment on the role of substrate surface in the interfacial structure. We will base our discussion on recent results concerning heteroepitaxial growth on Ge films on the Si(100) 2×1 surface.[17] Low-energy electron diffraction (LEED) patterns show that thin and thick Ge films deposited onto Si(100) 2×1 surface display a sharp 2×1 superstructure in contrast to the case of Ge on Si(111) 7×7 surfaces. This result suggests that the bond strength between Ge and Si is stronger on Si(100) surface than on Si(111) surface. We subsequently conclude that the substrate surface superstructure is more likely to survive growth conditions if the interfacial bond is stronger. This is indeed the trend we do observe when we study the stability of an interfacial superstructure in function of interfacial bond strength.[5]

In conclusion, we have discovered a new simple correlation between geometric and elastic-density factors, which enlightens our understanding of interfacial superstructure evolution, subsequent to modern epitaxial growth of films on crystalline substrate surface. This correlation demonstrates the role of strain in interfacial structural modifications. It implies a similarity between the geometric (G) and elastic-density (S) factors, as shown by the ratio $R \equiv S/G$ equals to 0.95, 1.01, and 1.06, respectively for Si/Ge, Si/$Ge_{0.5}Si_{0.5}$, and Si/SiO_2 coesite systems. A more extensive study is currently in progress.

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