Mechanical Stresses in (Sub) monolayer Epitaxial Films

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We have studied stresses in thin Ge films growing on Si(001), *in situ* and in real time, with submonolayer sensitivity. As a result of the 4.3% lattice mismatch, Ge films develop a compressive stress in the 2D growth regime, which saturates when 3D growth sets in. These measurements give new insight in the interatomic forces that play a dominant role in establishing the growth mode and the generation of defects, and provide a new test for state-of-the-art total-energy calculations.

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The growth mode of a thin epitaxial film is controlled by two factors. A necessary condition for wetting of the substrate by the overlayer is that the surface free energy of the overlayer is lower than that of the substrate. In this case the overlayer will initially form a continuous film. In order to sustain this simple growth mode it is imperative that the lattice mismatch between substrate and overlayer is sufficiently small to prevent the buildup of significant stress in the overlayer. If the stress becomes too large, the overlayer may form islands and/or defects may be generated at the interface or throughout the epitaxial film.

The relation between surface stress and surface structure has been studied experimentally by several authors, by varying the alloy composition of pseudomorphic epitaxial Ge/Si films on Si(111) (Refs. 1 and 2) or by applying an external stress to the sample,[3] but direct measurements of surface stress have not been reported previously, to our knowledge.

Theoretical calculations of surface stress for a number of adsorbate-induced 1×1 and $\sqrt{3}\times\sqrt{3}$ structures of the Si(111) surface were recently performed by Meade and Vanderbilt,[4] but, again, no experimental observations of such surface stresses have been reported.

Here we present a simple optical technique to determine stresses at surfaces and interfaces. This technique measures the bending of the substrate induced by the presence of surface stress and is sufficiently sensitive to detect stresses due to the adsorption of submonolayer quantities of adsorbates, in UHV and in real time. We believe that the technique, surface-stress-induced optical deflection (SSIOD), is a powerful tool to improve our understanding of the forces at work at surfaces and interfaces. Related techniques have been used to study stresses in thick films,[5] but to our knowledge this is the first time that such techniques are used in UHV and in the (sub)monolayer regime.

Briefly, if the stresses σ_1 and σ_2 present in the front and back surfaces of the sample are not equal, the sample will bend in order to minimize the stored strain energy. The resulting radius of curvature R derived after Stoney[6] is given by

$$R=\frac{Et^2}{6(1-\nu)(\sigma_1-\sigma_2)}, \tag{1}$$

where t is the sample thickness, E is Young's modulus, and ν is the Poisson ratio.[7,8] The angular deflection of the sample, τ, between two points separated by a distance d is given by $\tau=d/R$. By measuring this deflection, the difference $\sigma_1-\sigma_2$ is obtained from Eq. (1).

A schematic view of the setup is shown in Fig. 1. A thin sample is prepared in a U shape. In this study we used 0.1-mm-thick Si(001) samples, polished on both

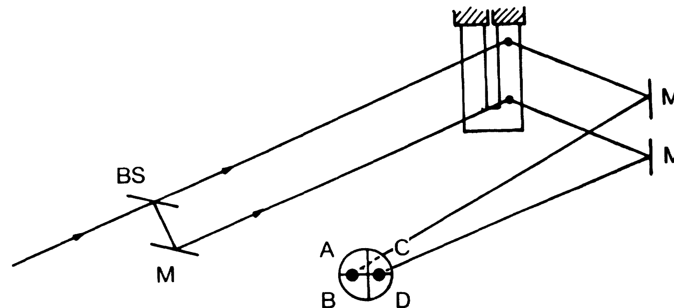

FIG. 1. Schematic setup of the experiment. M: mirror; BS: beam splitter; A,B,C,D: four-quadrant-split photodetector. For a full explanation, see text.

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sides (Virginia Semiconductors). The legs of the U are held in clamps which are electrically isolated from each other and from ground. Care has to be taken to ensure that the clamps are accurately parallel to each other to avoid distortion (and destruction) of the delicate sample. The Si sample is heated in UHV by direct current heating. First, sample and holder are outgassed thoroughly by heating the sample to 700 °C for many hours. Next, the sample is set at the temperature at which the experiment will be performed (500 °C in this work), and kept at that temperature for a few hours. The sample is cleaned by flashing off the oxide at 1050 °C for 30 sec. The temperature is then restored to the working temperature (500 °C), and the system is allowed to reach thermal equilibrium (approximately 1 h).

The incident He-Ne laser beam is split in two beams by a beam splitter (BS). One beam (the "reference beam") strikes the sample close to the clamp, and the other beam ("signal beam") is reflected by a mirror and strikes the sample close to the free end. The separation between the two beams on the sample is 8.4 mm. After reflection from the sample, the two beams are directed onto a four-quadrant-split photodiode, at a distance of 135 cm from the sample. The photodiode consists of four sectors, A, B, C, and D (see Fig. 1). The reference beam is incident on A and B; the signal beam on C and D. Both beams are chopped by a chopper in front of the beam splitter. A lock-in amplifier is used to measure the difference in signal strengths $[(C-D)-(A-B)]$, with an integrator time constant of 3 sec. If the sample bends, due to the presence of stress in the surface, the reference beam will be stationary, but the signal beam will be slightly displaced due to the sample curvature. This gives rise to a change in $C-D$, but not in $A-B$. Noise sources, such as vibration of the vacuum system, bending modes in the optical table, and some of the pointing instabilities of the laser, give rise to equal changes in $C-D$ and $A-B$. Thus, by subtracting these two difference signals a large gain is obtained in the signal-to-noise ratio. The vacuum system and the optical setup are placed on top of a conventional air-suspended optical table in order to reduce the sensitivity of the experiment to vibrations. With our current setup the noise corresponds to the equivalent of 1–2 μrad sample bending.

In recent studies of the epitaxial growth of Ge on Si(001) it was found that this system exhibits Stranski-Krastanov growth.[9] Initially, Ge forms a continuous film, but upon exceeding the critical thickness island formation occurs. This is due to the rather large lattice mismatch between Si and Ge (4.3% at 500 °C). The islands are relaxed to the Ge bulk lattice constant, with dislocations at the island/substrate interface. Thus, one would expect the buildup of a compressive stress in the thin Ge film (equivalent to a tensile stress exerted on the substrate) during the 2D growth phase, with little increase in stress during the 3D growth phase.

A sample with clean surfaces on both sides was prepared, as described above. Ge was evaporated from a carefully outgassed boron nitride Knudsen cell. The deflection signal was observed for some time before the initiation of growth. Then, at time zero, the shutter in front of the Knudsen cell was opened to expose the sample to the Ge flux, and the sample deflection was observed during growth. (We note that exposure of the sample to a hot, empty Knudsen cell does not result in a deflection. This excludes the possibility of sample-heating effects contributing to the signal.) Experimental results are shown in Fig. 2.

The sample starts to bend immediately upon opening of the shutter. Sample curvature increases quickly until it reaches saturation at a coverage of about 6 monolayers (ML). [Coverages were determined by Rutherford backscattering after the samples were removed from the UHV system and have an experimental uncertainty of $\pm 10\%$ (1 ML$=6.78\times10^{14}$ atoms/cm^2).] After the shutter is closed we find a small relaxation to smaller deflection over a time scale of several minutes.

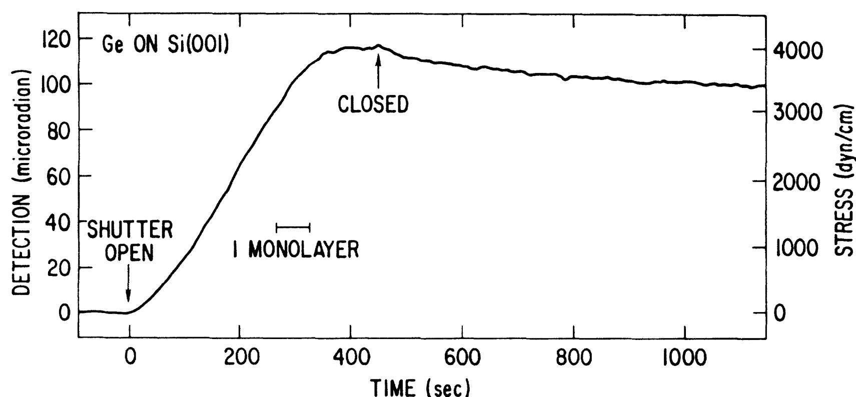

FIG. 2. Deflection signal measured during growth of a thin Ge film on Si(001) at 500 °C. The time needed to deposit 1 ML of Ge while the shutter was open is indicated.

The results presented here show a number of remarkable features. First, the sensitivity of the SSIOD technique is striking: Sample curvature due to the adsorption of as little as 0.1 ML of Ge can be observed. Second, although deflection occurs immediately upon opening of the shutter, the initial deflection rate is rather small. During these very initial stages of adsorption the Ge atoms are not yet constrained by the presence of additional Ge atoms in the immediate vicinity. Hamers *et al.* showed[10] that during the early stages of growth of Si on Si(001) 1D, isolated rows of dimers are formed. At higher coverage these rows coalesce into 2D monolayer-thick terraces. The initial nonlinear increase of the deflection signal indicates that large stress buildup occurs first during this coalescence phase, although a small stress is already observed prior to 2D coalescence.

Third, we have calculated the stress in units of dyn/cm by converting the substrate strain into the surface stress, using bulk elastic constants for the Si substrate. In the linear part of the stress buildup, between 2 and 4 ML, we measure the increase in stress to be 800 dyn/cm [corresponding to 0.73 eV/(1×1 unit cell)] per Ge monolayer. Linear elasticity theory predicts a value of 845 dyn/cm, per Ge monolayer, calculated for a bulk Ge sample with a 4.3% compression of the lattice parameters along both the [010] and [100] directions. Thus, even in these very thin films the elastic constants appear to be very close to the bulk value. We note that we do not directly measure the stress in the Ge film, but rather the difference in stress between the front and back surfaces. Since both surfaces exhibit the 2×1 dimer reconstruction, terminated with either Si or Ge, it is reasonable to assume that stresses associated with the dimer reconstruction are not too different for the two surfaces, and that the observed deflection is caused primarily by lattice mismatch. First-principles calculations of the stress in very thin Ge films on Si(001) are not available, but we believe that such calculations are feasible and that our data would provide an accurate test.

Finally, at higher coverages we observe the transition from 2D to 3D growth (islanding), with a saturation of stress buildup in the 3D growth regime. We find a small, but reproducible relaxation of the stress after closing the shutter, over a time scale of several minutes. There are two possible explanations for this relaxation. The small Ge islands may undergo Ostwald ripening, a phenomenon well documented for systems exhibiting Stranski-Krastanov growth.[11] Alternatively, interdiffusion is likely to occur at the Si(001)/Ge interface. Such interdiffusion was proposed in a recent Letter by Kelires and Tersoff, on theoretical grounds.[12] The dimer reconstruction gives rise to extensive strains in the subsurface region. Substitution of sites under compressive stress with Si, or of sites under tensile stress with Ge, will lead to a reduction in interface energy and stress. We have also observed this relaxation when growth was interrupted in the 2D growth regime, giving additional evidence for interfacial interdiffusion.

In conclusion, we have presented the first measurements of surface and interface stresses induced by monolayer and submonolayer quantities of adsorbates by surface-stress-induced optical deflection. We believe that this technique will allow us to improve our understanding of the mechanical stresses accompanying surface reconstruction and interface formation. For epitaxial systems with smaller lattice mismatch we anticipate that the reduction in overlayer stress associated with defect creation upon exceeding the critical thickness can be observed in real time.

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Note added.—Adsorption of As on Si(001) was studied in a similar fashion. At 500 °C adsorption saturates at a coverage of 1 ML. The As atoms form dimers in order to eliminate two dangling bonds per 2×1 unit cell. Each As atom carries a lone pair orbital. At 1-ML coverage we find a tensile stress of 1400 ± 100 dyn/cm relative to the clean Si(001) surface. This is in good qualitative agreement with the theoretical results of Meade and Vanderbilt for an As terminated Si(111) surface. The tensile stress is the result of the tendency of As to form 90° bond angles.[4]

It was found recently that As termination of the Si(001) surface changes the growth mode of Ge from Stranski-Krastanov to layer-by-layer.[9] Although this change in growth mode appears to be the result primarily of a reduction in surface mobility of the adsorbing Ge atoms, the tensile-stress contribution of the As layer offsets the compressive stress of the Ge film and thus helps to stabilize layer-by-layer growth. We believe that it also delays the generation of mismatch-related defects in the epitaxial Ge films.

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