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Nanostructure formation in the initial roughening of a thin silicon sheet

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Silicon-on-insulator (SOI) presents a unique model system for exploring the stability of crystalline nanomaterials in metastable configurations. We show that the initial destabilization of ultrathin SOI is related to mechanical stress, in contrast to phenomena at later times driven by the energy of the SiO_2/Si interface. Stepped rectangular truncated pyramids, with lateral dimensions of tens of nanometers, are formed on the outer Si layer of ultrathin (001)-oriented SOI during heating in ultrahigh vacuum. Pyramid edges are bounded by doubled atomic steps, with corners consisting of a complex series of single-layer steps. The shape of these nanopyramids represents a balance between stress-induced roughening and the elastic interaction between steps. SOI allows the precisely known energetics of silicon surfaces to be readily adapted to materials with nanoscale dimensions.

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The desirable properties of nanomaterials, including large surface areas, sharp interfaces, and precise mechanical distortion also make them metastable or unstable with respect to structural relaxation. The range of stability is commonly described using a continuum treatment to find configurations that reduce the overall free energy. The roughening of planar surfaces and interfaces, for example, can be understood using thermodynamic models to describe the competition between bulk and surface energies.[1] This approach applies equally well to crystalline solids and to molecular systems lacking long-range order.[2] The more complex perturbations necessitated by the discreteness of atomic-scale surface features on crystalline surfaces complicate the theoretical description of instabilities because energies associated with specific surface structures must be considered.[3] Here we describe atomic-scale structures formed on ultrathin silicon-on-insulator (SOI) and discuss the causes of their formation. SOI is a unique model system for investigating the evolution of metastable nanomaterials because it allows concepts from the surface science of Si (001) to be applied to an entirely new class of structures.

Ultrathin SOI consists of a template layer of crystalline Si bonded to a generally far thicker layer of SiO_2 supported in turn by a bulk Si wafer. The thinness of the template layer allows planar processing techniques to be used to form nanowires and other low-dimensional materials from SOI.[4–6] These SOI-derived nanostructures are highly promising from the standpoint of control of electronic, optical, and vibrational phenomena, including using surfaces and interfaces to control of the Si Fermi level.[7,8]

The stability of SOI and structures formed from SOI are understood under some circumstances but the atomic-scale mechanisms associated with the initial stages of degradation of SOI have not been described. Heating ultrathin SOI in ultrahigh vacuum for periods of minutes to hours produces isolated nanoparticles of oriented crystalline Si supported on the SiO_2 layer.[9,10] This phenomenon is driven by the low surface energy of SiO_2 in comparison with crystalline Si and always starts at defects in the Si template layer that reach the oxide.[9,11,12] We use scanning tunneling microscopy (STM) to show that there is an initial roughening of the Si template layer in which the roughening occurs uniformly across the surface with no preference for defect sites and for which the difference in surface energies between SiO_2 and Si is irrelevant. The buried SiO_2-Si interface is unchanged during this initial roughening and the process is thus independent of the SiO_2-Si interfacial energy.

The surface of a 15-nm-thick (001)-oriented Si template layer on a buried oxide layer on a (001) Si substrate was chemically cleaned and then hydrogen terminated by a 1 min exposure to 1% HF solution. Samples were loaded into ultrahigh vacuum and heated to 600 °C for several hours to remove water from the substrate and sample holder. The preparation of clean surfaces consisted of heating the sample from room temperature to 880–1000 °C in less than 10 s and leaving the sample at this temperature for a period of 10–90 s. The pressure during this process briefly reached a maximum of 1.0×10^{-9} Torr. The samples were cooled at a rate of 1 to 5 °C/s and subsequently imaged at room temperature using STM with a tip bias voltage of −1.5 V and a current of 0.5 nA.

Heating SOI in this way produces stepped pyramidal nanostructures, as shown in Fig. 1 in an image of a 40-nm-wide area of an SOI sample heated to 960 °C for 18 s. Pyramids have overall heights of 1–2 nm and top terraces and bases with lateral dimensions on the order of 10 and 50 nm, respectively. At larger lateral scales, the surface is tiled by a large number of contiguous, irregularly sized, truncated four-sided symmetric pyramids, with no long-range order. Such features are absent on bulk Si. The range of conditions under which nanostructures could be produced included longer times at lower temperatures, e.g., 90 s at 880 °C and shorter times at higher temperature, e.g., 10 s at 990 °C.

With the exception of a single terrace at the top of the pyramid, steps at the edges of the pyramidal structures are grouped into pairs, as in the cross section shown in Fig. 2. Steps are arranged so that parallel rows of dimers terminate at the terrace edges. This effect is illustrated in a small area near the corner of one pyramid shown in Fig. 3(a). Doubled steps at perpendicular edges of the nanostructure are offset in height by one atomic layer to allow each step to be perpendicular to the dimer rows of the terraces above and below it.

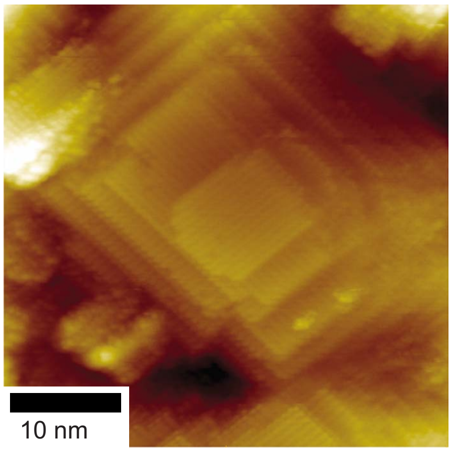

FIG. 1. (Color online) Nanostructures formed by annealing a 15-nm-thick (001)-oriented SOI template layer at 960 °C for 18 s and cooling at 1 °C/s.

Single-layer-high steps at each corner mesh the double-height steps of adjacent faces. The complex arrangement of single and double steps is shown schematically in Fig. 3(b).

Step doubling on bulk Si surfaces originates from the dependence of the elastic interactions between steps on the direction of the terrace edge relative to the dimer rows.[13,14] As a result double-height steps are formed on vicinal Si surfaces to allow rows of dimers to terminate at steps.[15] The kinetics of the redistribution of steps on surfaces has been widely studied in a number of bulk materials, and it is now understood that the energetically favored step arrangement will be reached rapidly in steeply stepped Si surfaces.[16] The arrangement of steps in Fig. 3(a) indicates that the surface has had sufficient time to reach an energetically favorable arrangement of steps with respect to the dimer rows by forming structures that minimize the number of unpaired steps and steps with higher energies.

The square or rectangular footprints of the pyramidal nanostructures arise from the anisotropy of the energy associated with forming steps on the Si surface. Forming steps along ⟨110⟩ directions with few kinks minimizes the step energy, as in the formation of long step facets between isolated kinks on azimuthally miscut bulk surfaces.[17] The corner structure in Fig. 3 allows nearly all of the steps surrounding the pyramid to be doubled, leaving only 2–4 dimer spacings of single-step edge at each corner. Only a few percent of the edge of each terrace consists of steps with the unfavorable orientation of dimers.

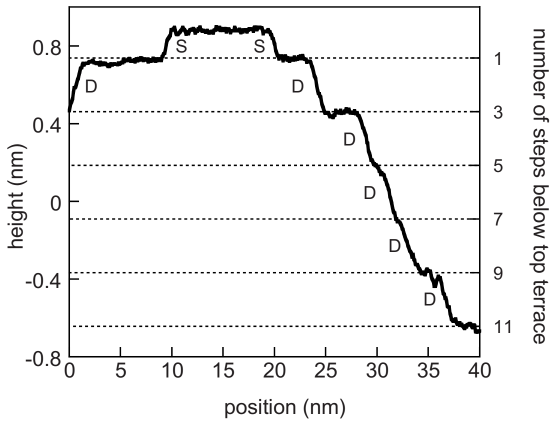

FIG. 2. Cross section of the truncated pyramid nanostructures formed on SOI. Double-height and single-height atomic steps are labeled D and S, respectively.

We hypothesize that the surface nanostructures formed by heating clean SOI result from the competition of two energetic considerations: elastic relaxation of mechanical strain in the SOI template layer by 3D structures, and the formation of a nanometer-scale arrangement of steps allowing the structures to form with minimum cost in surface energy. The resulting surface nanostructures have lattice constants closer to unstressed Si than the stressed SOI, but require the formation of additional surface features, including steps and corners. Stresses acting on the Si template layer of SOI can originate in the processing of the template layer or the SiO_2 buried oxide[18] or in stresses arising from thermal expansion. The strain in the Si template layer is elastically relieved by creating surface nanostructures once the temperature of the sample is sufficiently high to allow atomic motion across the surface. Similar phenomena occur during roughening of highly strained, but initially smooth, heteroepitaxial layers that are grown at low temperature and then heated, e.g., Ge or SiGe on Si (001).[19,20]

The stress required to produce a roughened template layer can be predicted by comparing the free energies of the Si surface before and after the formation of nanostructures. The rectangular stepped pyramids in Fig. 1 are geometrically similar to square pyramid structures for which the free energy has been calculated analytically.[3,19] The difference between the free energies of a flat surface and a surface with a pyramid bounded by stepped sides with lateral dimension $2s$ forming an angle θ with the substrate surface is[19]

$$\Delta G(s,\theta) = -6cs^3 \tan^2\theta + \frac{4s^2 \tan\theta}{h}\left[\lambda_0 + \lambda_d\left(\frac{a\tan\theta}{h}\right)^2\right]. \tag{1}$$

The first term in Eq. (1) represents the decrease in elastic energy resulting from the creation of the pyramid. Here $c = \sigma^2(1-\nu)/2\pi\mu$, h is the atomic-step height, a is the surface lattice constant, ν is the Poisson ratio, μ is the shear modulus, and σ is the stress in the template layer, which is assumed to be isotropic in the plane of the surface.[21] The second term describes the energy required to create the required steps, including step energy per unit length λ_0 and the energy per unit length of elastic repulsion between steps, λ_d.[19]

The critical stress at which ΔG vanishes is plotted in Fig. 4(a) for a wide range of the full widths $2s$ of islands. When the stress is higher than the critical stress ΔG is negative and it is energetically favorable to form pyramids. The plot in Fig. 4(a) is based on bulk elastic constants,[22] the experimentally observed θ, 6°, and values of the step parameters from the heteroepitaxy of Ge on Si.[19] These step energies provide a self-consistent starting point for understanding roughening into pyramidal structures. Similar values of the critical stress are obtained for step energy values determined using other

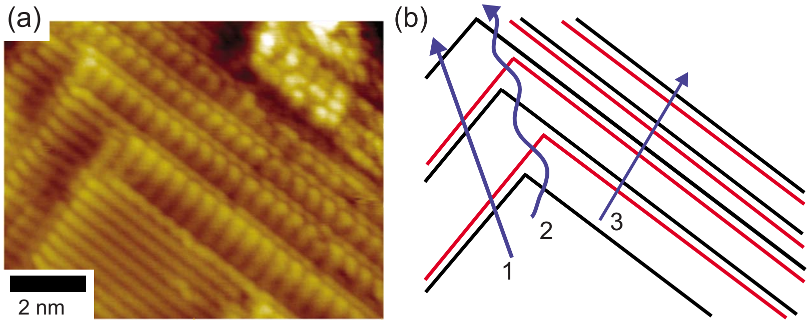

FIG. 3. (Color online) (a) A corner of a nanostructure formed by annealing a SOI(001) template layer at 960 °C for 18 s and cooling at 1 °C/s. (b) Schematic diagram illustrating the arrangement of steps. Lines 1 and 3 indicate the sequence of double-height steps from the top terrace along its edges. Line 2 shows the sequence of single-height steps at the corner.

experimental and theoretical approaches.[14] Using the values from Ref. 19 in Eq. (1), it is energetically favorable to create stepped pyramids with dimensions similar to those of the structures shown in Fig. 1 when the biaxial stress exceeds approximately 1.9 GPa. This critical stress is very high, equivalent to a biaxial strain on the order of 1%.

The biaxial strain in the Si template layer was measured by using low-energy electron microscopy (LEEM) to determine the density of dislocations resulting from stress relaxation at high temperature. LEEM images individual dislocations via the large domains of preferential dimer orientations resulting from the stress field of the dislocation.[23] Figure 4(b) is a dark-field LEEM image of a 100-nm-thick Si template layer that was rapidly heated from 650 to 1200 °C and quenched to 650 °C in a total of 5 s. The linear dislocation density η after annealing is approximately 1 μm^{-1}. Pyramids formed on the Si template layer would not change the LEEM image, as individual steps are not resolved in Fig. 4(b). The stress relieved by an array of dislocations in which the Burgers vector projects a length b onto the plane of the surface is $\frac{E}{(1-\nu)}\eta b$, where E is the bulk modulus. With $b=0.193$ nm for the relevant slip system in Si (001),[24] the stress relaxed by dislocations in 100-nm-thick template layer is 40 MPa.

When a constant interface stress is applied at the template layer/SiO_2 interface, the average stress in the template layer is inversely proportional the template layer thickness. The stress in a 15-nm-thick SOI layer would be between 6 and 7 times higher than in 100 nm template layer shown in Fig. 4(b), or on the order of 250 MPa. Literature values of the stress in ultrathin SOI vary widely. Extrapolating from thick SOI layers, Tiberj *et al.* estimated that the stresses in ultrathin SOI are on the order of 50 MPa.[18] Tang *et al.* reported stresses of up to 300 MPa in 3-nm-thick layers and lower values in thicker 10-nm-thick SOI.[25] These stresses correspond to a biaxial strain in the Si template layer of at most 0.2%.

We now consider the possible origins of the difference between experimentally obtained stresses in the Si template layer and the critical stress predicted using Eq. (1). First, the predicted critical stress depends strongly on λ_0 and λ_d, and thus changes in the surface energetic parameters would change the predicted critical stress. Forcing ΔG to vanish for the pyramids shown in Fig. 1, however, would require a reduction of the step energies to unphysically low values of approximately 5% of those that have been previously measured.[19] A small error in step energy parameters thus does not seem to be the origin of the difference between the experimentally observed stress and the predicted critical stress.

A more likely origin for the difference between our experimentally estimated stresses and the predicted critical stress lies in the mechanical assumptions leading to Eq. (1), and in the possibility that the measured values of stresses underestimate the stress at high temperatures. The pyramidal model leading to Eq. (1) considers a different elastic configuration than the truncated pyramid nanostructures on SOI. The most important aspects of an improved elastic description would be to account for the low shear modulus μ of SiO_2, the layered SOI structure, and the flat terraces at the tops of the pyramids. Softer substrate elastic coefficients affect elastic-energy term in Eq. (1) by producing in a larger net elastic-energy release when the pyramids are formed. The large strain induced in the analogous situation of nanostructure formation in Ge/Si epitaxy, for example, results in large-scale deformation of the SiO_2.[26] A mechanical description accounting for the difference between the semi-infinite substrate assumed in the derivation of Eq. (1) and the layered structure of ultrathin SOI is not yet available.

The origin of stress in ultrathin SOI is poorly understood from an experimental perspective, particularly at elevated temperatures. *In situ* stress (or strain) measurements at high

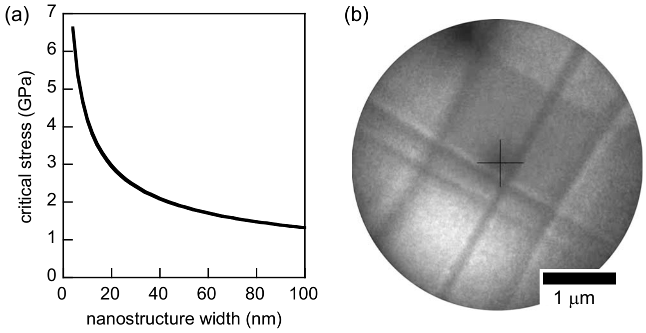

FIG. 4. (a) The critical stress for the formation of stepped-pyramid nanostructures with the experimentally observed sidewall angles as a function of their full width $2s$ predicted using Eq. (1). The values of the step energies are,[19] $\lambda_0=2.7$ meV/Å and $\lambda_d=4.4$ meV/Å. (b) A dark-field LEEM image obtained using the (1/2 0) reflection at an electron-beam energy of 10 eV showing the formation of dislocations in a 100-nm-thick SOI(001) template layer during thermal annealing. Each bright-dark pair of straight lines is the signature at the outer surface of a dislocation in the Si template layer.

temperatures would allow far more precise comparison between elastic models and experiments than is presently possible. Such measurements could also potentially elucidate novel origins of stress, such as large-scale mechanical movement at the highly stressed SiO_2/Si substrate interface. Slip at this interface would allow large temperature-dependent stresses originating from the difference in thermal expansion between SiO_2 and Si to be transmitted to the template layer at high temperatures.

In summary, the early stage of the roughening of the template layer of SOI produces atomic-scale structures with shapes determined by the energetics of steps. Later stages amplify these initial structures by effects such as the development of crystallographic facets and the exposure of large areas of SiO_2, as chemical interfacial-energy differences become important. The precision with which the Si surface can be prepared and studied theoretically makes SOI and SOI-derived nanostructures an excellent model system for quantitative studies of the stability of supported and free-standing nanomaterials.

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