Summary Abstract: Epitaxy of monolayer silicon films studied by optical second-harmonic generation

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The epitaxial rearrangement of adatoms on growing surfaces is fundamental to molecular beam epitaxy. The primary process by which this occurs is believed to be the migration of adatoms to more stable kink positions in the step train that exists on the surface. Information on the kinetics of such epitaxial reordering, even on a technologically important material such as silicon, is however, quite limited. In this work, we investigated the ordering of well-characterized silicon surfaces during the molecular beam deposition of Si at various substrate temperatures and during the annealing of amorphous Si films of monolayer thickness. These measurements were performed in real time using the nonlinear optical technique of second-harmonic generation (SHG).

The noninvasive optical probe of SHG can provide information on the condition of surfaces and interfaces with monolayer sensitivity.[1] The surface specificity of this technique is present for centrosymmetric media where SHG is forbidden (under the electric-dipole approximation) in the bulk, but is allowed at the surface where the symmetry is broken. Previous applications of SHG method have included investigations of Si(111)-2×1 and -7×7 surfaces and of the phase transformation between these two reconstructions.[2] When the measurements are performed with pump laser radiation directed onto the sample at normal incidence, SHG is possible only if the sample exhibits long-range order. Consequently, the SH signal in this configuration can provide an effective means of assessing the degree of crystallinity of the surface.[3]

Our measurements were conducted on Si(111)-7×7 surfaces prepared in a standard ultrahigh vacuum system equipped with a resistively heated Si filament for Si deposition. The order and cleanliness of the sample could be determined by low-energy electron diffraction (LEED) and Auger spectroscopy. The SH signal was produced with normally incident pump radiation from a Q-switched Nd:YAG (Nd-doped yttrium aluminum garnet) laser operating at a wavelength of 1.06 μm. The experimental apparatus permitted changes in surface structure to be monitored on the time scale of seconds. For deposition of Si on a Si(111)-7×7 surface held at elevated temperatures, we observed the anticipated constant SH response associated with epitaxial growth. For deposition at room temperature, however, the second harmonic field decayed exponentially. This behavior is expected for the case of the development of a disordered film from immobile adatoms. The LEED structure was also seen to be disrupted. From analysis of these data, we were able to deduce a value for the area of the surface perturbed by an adatom, as reflected in the surface electronic properties governing the SHG process.

To investigate the kinetics of the crystallization process, a disordered Si adlayer of ~1.5-Å thickness was formed by room-temperature deposition. These films were annealed at a constant temperature, which could be rapidly obtained by means of resistive heating of the substrate. The change in surface structure was monitored by the SH intensity. The eventual ordering of the surface was also verified by the reemergence of the LEED pattern. For substrate temperatures in the range of 500–700 °C, we found the initial reordering of the surface to be an activated process. The activation energy deduced from these studies was 1.2 ± 0.2 eV. In previous analyses of steady state growth during Si molecular beam epitaxy, an upper bound of 0.2 eV was inferred in the early work of Abbink *et al.*[4] and, more recently, a less stringent upper bound of 1.1 eV was found by Kasper[5] for the activation energy associated with adatom diffusion. A more direct comparison can be made with the work of Bedair[6] on a slightly different physical system consisting of a Si(111)-7×7 surface disordered by intense pulsed laser radiation. For this case, measurement of the evolution of a fractional order LEED spot yielded an activation energy of 1.1 eV, similar to our result for a disordered adlayer. The theoretical predictions of NoorBatcha *et al.*[7] based on classical trajectory methods strongly underestimate our experimental results; the figure of 0.8 eV for the energy barrier for adatom motion on an ideal Si(111) surface obtained by Northrop and Cohen[8] from pseudopotential calculations is in closer agreement. For comparison, the activation energy for solid phase epitaxial regrowth of thick amorphous films is in excess of 2 eV.[9]

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