Layer-by-Layer Sputtering and Epitaxy of Si(100)

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We report oscillations in diffracted electron intensities during ion bombardment of Si(100) by 200- and 250-eV Xe, both alone and with sequential and simultaneous epitaxy. Analysis of the phase and frequency of the oscillations shows that, to first order, ion bombardment "undoes" previous epitaxy and cancels or partially cancels simultaneous deposition. Surprisingly, the phase relationship of growth and sputtering is both antisymmetric *and* linear, indicating that the ion-induced oscillations are dominated by simple, vacancy-mediated, layer-by-layer sputtering.

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The modification of semiconductor surface morphology under bombardment by relatively low-energy (<400 eV) noble-gas ions has recently attracted wide interest [1], in part as a result of efforts to alter growth kinetics in MBE (molecular-beam epitaxy) using ion beams [2-4]. Recent simulations have suggested that the damage induced by lower-energy ions (<100 eV) is confined to a very few atomic layers near the surface [5], avoiding the collision cascades and substantial bulk damage associated with higher-energy ions [6]. For a metal surface, layer-by-layer atom removal during 600-eV Ar^+ irradiation of Pt(111) has been reported from thermal-energy atom scattering (TEAS) [7].

Even if the ions interacted primarily with the surface, however, the manner in which low-energy ions affect growth kinetics and surface morphology might still be quite complicated. Indeed, this interaction has been associated with a combination of complex mechanisms, including cluster destabilization, surface defect formation, enhanced adatom diffusivity and nucleation, and preferential sputtering of chemically or structurally different surface atoms [2].

In this Letter, we report what we believe to be the first observation of RHEED (reflected high-energy electron diffraction) oscillations during sputtering of a semiconductor surface, demonstrating layer-by-layer removal as has been reported for a metal [7]. In addition, we find that the phase of these oscillations scales linearly with prior silicon deposition. Third, we find that the frequency of epitaxial-*growth* oscillations can be altered by simultaneous ion bombardment, with the resulting RHEED frequency given simply by the difference in rates of deposition and ion-induced atom removal. In agreement with the metal studies [7], we show that these results are consistent with a *simple* picture in which ions create mobile vacancies, which annihilate adatoms one for one.

The chamber used for these experiments has been described previously [8]. Silicon is deposited from a commercial electron-beam source, and an electron-impact ion gun is fixed 15 cm from the sample and oriented 60° from the surface normal. The $4\times6\times0.5$-mm Si substrates are (100) oriented within 0.05°, as determined by x-ray diffraction and the position of the RHEED shadow [9]. Sample temperatures are recorded from a W-5%Re/W-26%Re thermocouple placed in a 0.175-mm hole drilled in the side of the sample.

The samples are initially cleaned chemically [10] and then transferred immediately to the vacuum chamber. A sharp 2×1 diffraction pattern is obtained by heating the sample at 800 °C while depositing silicon at a rate of 1 ± 0.1 ML/min (ML denotes monolayer) for 20 min. In order to remove any residual roughness created in subsequent growth or ion exposures, we normalize the starting condition for each exposure by heating the sample at 850 °C for 1 min and depositing 10 ± 1 ML of silicon at 750 °C and 1 ML/min.

In order to monitor the evolution of the surface morphology, the 15-keV RHEED intensity resulting from the diffracted electrons striking a phosphor screen is measured with a charge-coupled-device camera. RHEED has been widely used as a diagnostic of the epitaxial-growth process by virtue of its straightforward implementation and real-time measurement capability [11-13]. We measure the evolution of the intensity of the specular beam in the "out-of-phase" condition, which has been shown to be particularly sensitive to surface roughness because of the destructive interference of scattered beams from terraces separated by a single atomic step [14]. In this work, the RHEED beam is oriented 8° off the ⟨110⟩ azimuth to suppress Kikuchi band interference [14]. Because of the complexity of interpreting RHEED intensities quantitatively, we do not attempt here to compare absolute intensities between different growth or sputter sequences; we use only relative intensities during a single growth or ion exposure and compare only periodicities between different exposures.

After the surface preparation described above, epitaxial silicon growth yields temporal oscillations in the out-of-phase, specular intensity [13], and we use the persistence and strength of these oscillations to evaluate the smoothness and cleanliness of the starting surface. Figure 1 shows the results of 200-eV Xe exposure of Si(100) to an ion flux of 1.2 ± 0.4 $\mu A/cm^2$ estimated from a Faraday-cup measurement. At the elevated temperatures shown (510 and 470 °C), ion bombardment results in a monotonic decay of the RHEED intensity, without per-

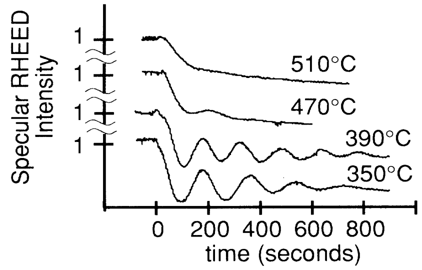

FIG. 1. Specular RHEED intensity evolution in the out-of-phase condition during 200-eV Xe bombardment of Si(100), at the substrate tempertures indicated. The offset plots have the same scale and are normalized to unity at $t=0$, when Xe exposure begins. Variations in the RHEED frequency between traces are dominated by long-term drift of the ion flux.

sistent oscillations. At the lower temperatures, pronounced intensity oscillations are observed. While the oscillations damp within a few cycles, a well-defined period can be identified in each case; the small variation in periods reflects actual, unintended variations in ion flux.

This pattern of temperature dependence is widely encountered in semiconductor epitaxy, where oscillations in the specular RHEED intensity result from the periodic filling of each new layer, as adatom diffusion promotes layer-by-layer growth through nucleation and coalescence of islands. Increasing the substrate temperature and adatom mobility suppresses the RHEED oscillations when either (a) the size of the deposited islands exceeds the transfer width of the diffraction instrument [7] or (b) the density of nuclei falls below the average density of steps that results naturally from the specific surface misorientation, so that growth is then dominated by the flow of steps, which act as sinks for deposited adatoms [9].

The correspondence of the sputtering data in Fig. 1 with this general picture of epitaxy confirms that the processes underlying ion-induced oscillations are also mediated by mobile defects which nucleate and ripen defect clusters [15]. It remains to describe the nature of the defects.

In order to address this question, we expose initially smooth surfaces to ion bombardment immediately after a submonolayer silicon deposition. Figure 2(a) shows a sequence of ion-induced oscillations following deposition of up to $\frac{3}{4}$ ML Si. A partial oscillation is observed during the growth, and the switch from growth to ion bombardment causes in each case an immediate reversal of the direction of the evolution of the RHEED intensity. The slope of the curves of intensity versus deposition or ion fluence in Fig. 2(a) is related to the rate of production of two-layer roughness on the miscut terraces. As the slope of these curves switches sign when deposition is replaced by ion bombardment, the rate of production of two-layer roughness is simply being reversed.

In each case, the final phase of the initial growth oscillation, defined as the fraction of a cycle between the initial exposure and the switch from deposition to ion bombardment, is opposite to the initial phase of the ion-induced oscillations, defined as the fraction of a cycle between the initial ion exposure and the subsequent intensity maximum. This observed antisymmetry of the phases of growth- and ion-induced oscillations indicates that ion exposure removes clusters formed during prior Si deposition. Such a process could be achieved, for example, by one-for-one annihilation of a mobile vacancy created by the Xe bombardment with a cluster edge atom or an adatom evaporated from an island edge, as shown by our own Monte Carlo simulations [16]. If the ion-surface interactions were mediated instead by adatoms created in the sputtering process, as by ejection from the bulk or from terrace edges, then the phase reversal would not be expected.

If Si removal by sputtering leaves behind mobile vacancies which recombine with adatoms, then the number of vacancies required to "annihilate" the previously deposited Si and create an atomically smooth surface would be proportional to the quantity of predeposited Si. The phase relationship between growth- and ion-induced oscil-

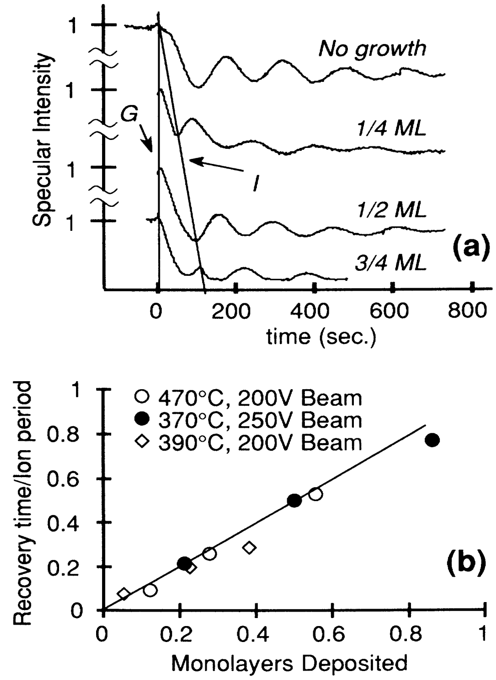

FIG. 2. (a) Evolution of the RHEED intensity under 250-eV Xe bombardment of Si(100) at $T=370\,^{\circ}\mathrm{C}$, following Si deposition as indicated. Growth is initiated at $t=0$ in each case (line G). The line labeled I indicates termination of growth and initiation of Xe bombardment. (b) Plot of the time from ion exposure to the first RHEED maximum, normalized to the ion-induced oscillation frequency, the quantity of prior Si deposition, for surfaces exposed to ion bombardment following submonolayer Si deposition as in (a). Exact phase reversal from deposition to sputtering would lead to the line of unit slope shown.

lations should then be linear as well as antisymmetric. Indeed, Fig. 2(b) illustrates this direct proportionality, over a range of substrate temperatures, between the quantity of predeposited silicon and the time between the initial ion exposure and the next oscillation maximum. We note that while the absolute RHEED oscillation phase depends on the incident electron-beam angle [17], Fig. 2(b) compares relative phases with a fixed RHEED geometry.

The results in Fig. 1 for ion exposure on a smooth surface are consistent with this picture. For the two lower temperatures represented, vacancy diffusion would result in the nucleation of vacancy clusters, and the sequential removal of layers would give rise to the oscillations. At the higher temperatures shown, the elevated mobility of vacancies would enable them to reach step edges, and silicon removal would then proceed by adatom-vacancy annihilation at step edges. The oscillations would be suppressed as in the case of growth at elevated tempertures.

In order to establish the precise quantity of silicon removed during one ion-induced oscillation period, we investigate the interaction of the Xe^+ beam with a dynamic surface, by exposing an initially smooth substrate to simultaneous deposition and Xe bombardment. As shown in Fig. 3, the resulting RHEED frequency equals the difference between the frequencies that would result from either growth or sputtering alone. The oscillations are eliminated [Fig. 3(a)] when the two component frequencies match. Therefore, the Xe beam can effectively reduce and even eliminate the *net* Si deposition. The periods of the growth oscillations in each figure above have been identified with single-monolayer deposition by crystal

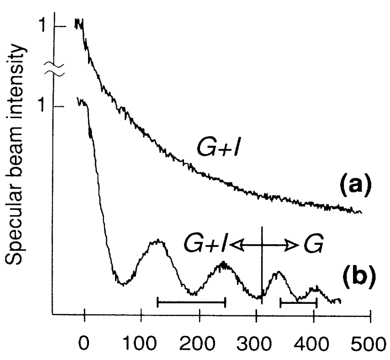

FIG. 3. Evolution of the RHEED intensity during simultaneous Si deposition and Xe bombardment with the substrate at 380 °C. In (a), the oscillation frequency of either component alone would be 0.006 s^{-1}. In (b), the growth component is 0.015 s^{-1}, and the ion component is 0.006 s^{-1}. Deposition and growth together $(G+I)$ result in oscillations at 0.009 s^{-1}, and termination of the ion beam (G) gives oscillations at the growth frequency. The solid bars beneath the plot display the respective periods.

monitor calibration, so the cancellation of oscillations under the conditions of Fig. 3 establishes the correspondence of an ion-induced oscillation with the removal of one monolayer. RHEED, like TEAS [7], can therefore be used to measure orientation-specific sputter rates. The already widespread use of RHEED in semiconductor MBE enables routine use of RHEED oscillations in sputter-rate measurements for semiconductors.

Finally, we observe ion- and growth-induced RHEED oscillations at comparable rates over comparable temperature ranges, suggesting that adatom and vacancy mobilities are similar. In fact, Monte Carlo simulations of simultaneous epitaxy and ion bombardment (details in Ref. [16]) reproduced our main experimental observations best when the near equality of the two defect mobilities was assumed. We suggest that a quantitative, experimental investigation of vacancy mobilities would therefore offer fundamental parameters underlying defect-mediated atom removal and rearrangement.

We observe from Fig. 3 a decay envelope in the RHEED intensity, indicating that atomic redistribution with a monotonically increasing roughness persists even with zero or near-zero *net* Si deposition. In this case, adatom-vacancy annihilation, which would tend to smoothen a surface locally, must compete with both adatom and vacancy nucleation, tending to roughen the surface. In the first process, the two defects could cancel each others' contributions to the RHEED intensity, but any hindrance of this cancellation by defect nucleation on multiple layers would cause the overall multilayer roughness to persist even without net growth or removal. Our results suggest that the ability to influence the competition between microscopic processes by adjusting various deposition and sputtering parameters offers an opportunity for the purposeful redistribution of surface atoms to promote or eliminate a specific defect type, step density, or other specific structure that may not be readily accessible by growth alone. As the feasibility of applying scanning tunneling microscopy (STM) to examine atomic redistributions caused by sputtering has already been demonstrated [18–20], we suggest that further study of the generation and stability of the induced structures in the present system with a microscopic probe, for example, STM or surface x-ray diffraction, would illuminate the atomic redistributions caused by growth and sputtering.

In conclusion, we have found that (i) RHEED oscillations result from sputtering a Si(100) surface, (ii) ion bombardment removes prior growth, with a phase relationship between growth and subsequent ion bombardment that is linear with respect to the initial growth fluence, and (iii) simultaneous growth and sputtering results in a RHEED oscillation frequency equal to the difference of the frequencies produced by deposition and sputtering alone. The results of combining Si epitaxy and sputtering support a picture of ion-surface interaction, in the present ion energy regime, dominated by surface vacancy creation, migration, and nucleation, without a need to invoke more complex processes. It is surprising and remarkable that such "reverse epitaxy," found on a metal [7], could occur also for a semiconductor surface, with its tendency to reconstruct, reduced adatom mobility compared with a metal, amorphization under ion bombardment, and highly stressed covalent bonds.

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