

***In situ* monitoring of ion sputtering and thermal annealing of crystalline surfaces using an oblique-incidence optical reflectance difference method**

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We demonstrate that the morphology of crystalline surfaces during ion sputtering and thermal annealing can be monitored *in situ* with an oblique-incidence polarization-modulated optical reflectance difference technique. Such a technique is effective under high ambient pressures as well as ultrahigh vacuum. We studied the Ne ion sputtering and thermal annealing of Ni(111) from 623 to 823 K. We found that the rate-limiting step (with an activation energy of 1.1 eV/atom) during annealing is most likely to be direct evaporation of Ni atoms from step edges. © 1998 American Institute of Physics. [S0003-6951(98)00945-0]

The combination of ion sputtering and subsequent thermal annealing is the most common method to produce clean crystalline surfaces under suitable vacuum conditions before further material deposition and processing. In thin film epitaxy, thermal annealing of as-grown materials is a crucial step for producing high quality epitaxial films with atomically sharp interfaces. Since most new materials are made of multiple films of different materials of which some are as thin as a few atomic layers, it is most important that *thermal annealing is complete and yet not excessive*. An excessive thermal treatment (e.g., excessively high annealing temperature or long annealing time) can cause significant interdiffusion and intermixing between layers of different materials and thus widen the interfaces much beyond one atomic layer. It is thus desirable that one monitors the morphology of the surface under investigation *in situ* during ion sputtering and thermal annealing. And such a monitoring technique should be useful under the conditions of material deposition and processing as well as ultrahigh vacuum.

In this letter, we demonstrate that an oblique-incidence polarization-modulated optical reflectance difference technique can be used as such an *in situ* monitoring probe.^{1,2} Specifically, we report a study of the Ni(111) surface morphology during Ne ion sputtering and subsequent thermal annealing using such a technique. In these processes, the atomic composition of the outermost layer remains while the arrangement of the atoms changes. The optical reflectance difference signal detects such a change.

The experiment is conducted with a 1 cm² Ni(111) sample disk placed in an ultrahigh vacuum chamber. The base pressure during experiment is around 2×10^{-10} Torr. The surface of the sample is cleaned with short cycles of Ne⁺ ion sputtering followed by annealing for a few seconds at 1100 K. We can vary the sample temperature from 28 to 1500 K within ± 0.3 K. For the sputtering experiment, we back fill the chamber with 3.7×10^{-6} Torr Ne gas. We use a Perkin-Elmer PHI 04-161 sputter ion gun to produce the Ne⁺ ion beam. The ion energy is set to be 1.0 keV and the current on the 1 cm² Ni(111) sample is determined to be (3 ± 1)

$\times 10^{-8}$ A. This gives an ion impinging rate of $(2 \pm 0.7) \times 10^{11}$ ions/cm² s. From the reported studies of Michely and Comsa,³ we expect each Ne ion to remove or dislocate two Ni surface atoms so that the sputtering rate in our experiment is roughly $R = 4 \times 10^{11}$ Ni atoms/cm² s. In each measurement, we left the ion current on for 15 min or $t = 900$ s. This gives a total sputtering dose of $Rt = 3.6 \times 10^{14}$ Ni atoms/cm², roughly 0.2 ML for Ni(111).

For the oblique-incidence polarization-modulated optical reflectance difference measurement, we use the same setup and the detection method as described previously by Wong and Zhu and by Zhu *et al.*^{1,2} Before sputtering, we nullify the initial optical reflectance difference. The subsequent change in the detected reflectance difference $S(t)$ upon ion sputtering and thermal annealing is directly proportional to

$$\text{Re}[(r_p - r_{p0})/r_{p0} - (r_s - r_{s0})/r_{s0}] \equiv \text{Re}(\Delta r_p/r_{p0} - \Delta r_s/r_{s0}).$$

In Fig. 1, we display the optical reflectance difference signals $S(t)$ over 15 min of sputtering with the sample at

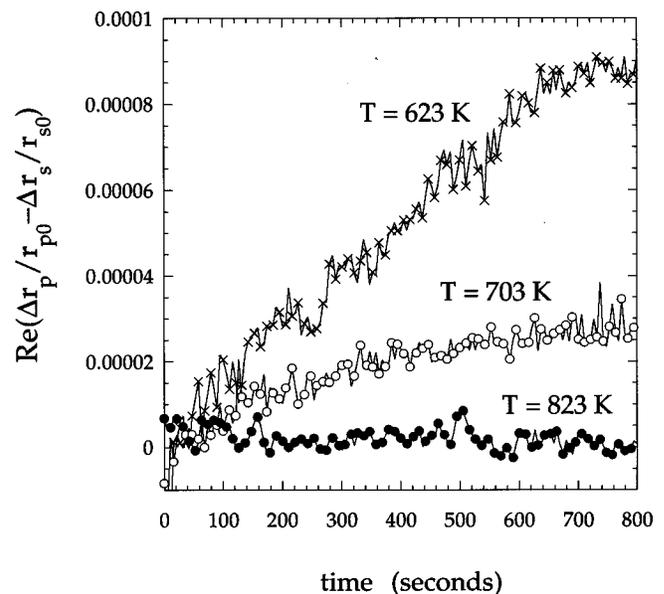


FIG. 1. Optical reflectance difference signals during 15 min Ne ion sputtering at a sputtering rate of $R = 4 \times 10^{11}$ Ni atoms/cm² s.

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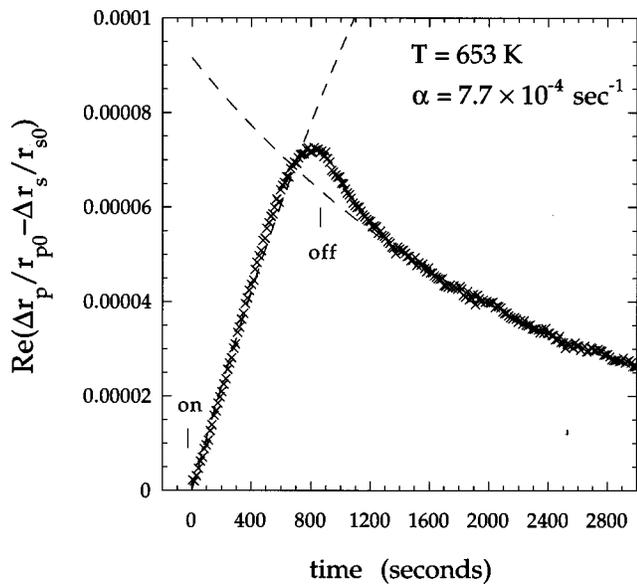


FIG. 2. Optical reflectance difference signal during a 15 min sputtering followed by thermal annealing at $T=653$ K. The dashed line during annealing alone is a fit to a single exponential function with an exponent $\alpha = 7.7 \times 10^{-4} \text{ s}^{-1}$. The dashed line during sputtering is calculated using the same exponent.

623, 703, and 823 K, respectively. The data sampling rate is 1 Hz. At $T=623$ K, $S(t)$ changes monotonically as a result of the sputtering-induced morphology change. As the sample temperature increases, the rate of change for $S(t)$ decreases due to the concomitant thermal annealing. At $T=823$ K and above, $S(t)$ no longer changes during sputtering. This indicates that annealing at this temperature is so efficient that the change in the surface morphology caused by sputtering is mostly recovered within the time interval of the sampling, namely, 1 s. We will call this temperature the critical annealing temperature at which the thermal annealing of an ion sputtered surface is complete within 1 s or thereabouts. This temperature is 70° below the suggested annealing temperature of 900 K in the literature⁴ and the annealing time is only a few seconds at 823 K rather than 15 min at 900 K as suggested in the same literature.

To further explore the kinetics of the annealing, we have monitored both the sputtering and the recovery (when the ion current is turned off). When the sputtering is off, the surface morphology is restored to the pre-sputtering state by annealing.^{3,5} In Fig. 2, we display the reflectance difference signal taken at $T=653$ K. Shortly after the sputtering is turned off, the recovery is fairly well characterized by a single exponential decay. We fit the reflectance difference signal during the recovery with a single exponential function. In Fig. 3, we show the Arrhenius plot of the recovery rates $\alpha(T)$ in the temperature range from 623 to 723 K. Assuming that $\alpha(T)$ has the form of $\alpha_0 \exp(-E_a/k_B T)$, we obtain an activation energy of $E_a = 1.1$ eV/atom or 25 kcal/mol that characterizes the rate of the annealing.

We now examine the detail of the surface morphology of Ni(111) during ion sputtering and annealing and its relationship to the optical reflectance difference signal.² The net result of sputtering increases vacancy and overlayer islands on the surface. The thermal annealing reduces these islands through three kinetics processes: (1) the evaporation of at-

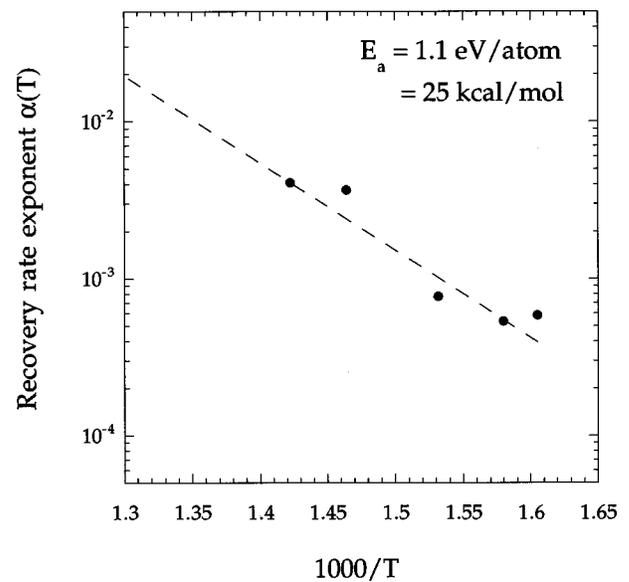


FIG. 3. Arrhenius plot of the recovery rate exponent α . The dashed line is a fit to $\alpha_0 \exp(-E_a/k_B T)$ with $E_a = 1.1$ eV/atom.

oms from edges of overlayer islands and of those vacancy islands that contain smaller vacancy islands; (2) the subsequent diffusion of these atoms across terraces to upper edges of vacancy islands; and (3) the descent of these atoms to lower edges of vacancy islands.^{6,7} During sputtering and/or annealing, the total number of surface atoms remains unchanged while the number of the atoms at step edges changes at the expense of those atoms inside terraces or vice versa. We thus expect the optical reflectance difference signal $S(t)$ to come from the difference in optical polarizability between a step edge Ni atom and a terrace Ni atom and to be proportional to the density of the additional step edge atoms $\Delta\theta_{\text{edge}} \equiv \theta_{\text{edge}} - \theta_{\text{edge},0}$ due to sputtering or incomplete thermal annealing.² $\theta_{\text{edge},0}$ is the equilibrium density of the step edge atoms when the surface is fully annealed and is determined by the initial mis-cut angle. The ion sputtering causes $\Delta\theta_{\text{edge}}$ to increase at a rate of R . The thermal annealing causes $\Delta\theta_{\text{edge}}$ to decrease. Since the observed recovery is described well by a single exponential function, the rate of change for $\Delta\theta_{\text{edge}}$ due to annealing can be expressed as $-\alpha\Delta\theta_{\text{edge}}$. Therefore we have $d(\Delta\theta_{\text{edge}})/dt = -\alpha\Delta\theta_{\text{edge}}$ during annealing alone, and we expect $S(t) = S(0)\exp(-\alpha t)$. During the ion sputtering, we have instead $d(\Delta\theta_{\text{edge}})/dt = R - \alpha\Delta\theta_{\text{edge}}$ and $S(t) = c'(R/\alpha)[1 - \exp(-\alpha t)]$ where c' is a constant. If this model is correct, the recovery exponent α obtained from the optical signal during annealing should also describe the optical signal during sputtering. In Fig. 2, we show the calculated optical reflectance difference signal during sputtering by using the recovery exponent obtained from the annealing or recovery part of the signal. The calculation agrees with the measurement very well.

From the measured activation energy of $E_a = 1.1$ eV/atom, we may deduce the rate-limiting step during thermal annealing out of the three kinetics processes mentioned earlier. In a scanning tunneling microscopy study, Müller and co-workers determined the diffusion energy barrier for Cu on Ni(100) to be 0.35 eV/atom and found it essentially the same as that on Cu(100).^{8,9} This suggests that

the binding energies for a Cu or Ni adatom on Ni and Cu surfaces are most likely determined by the number of chemical bonds formed with its nearest neighbors with a roughly constant single-bond energy. The measured diffusion energy barriers on (100) terraces of Ni and Cu are then simply the energies to break two bonds when a Cu atom hops from a fourfold coordinated hollow site to another over a twofold coordinated bridge site. Assuming that the same rule holds, we should expect the self-diffusion energy barrier on (111) terraces of Ni to be around 0.2 eV/atom as a Ni atom hops from a threefold coordinated hollow site to another over a twofold coordinated bridge site thereby breaking only one bond. It is a factor of 5 smaller than 1.1 eV/atom. As a result, the diffusion across terraces is not likely to be the rate-limiting process. By the same consideration, neither will be the descent of Ni atoms to vacancy islands as it involves a Ni atom hopping from a threefold site at the edge of an upper terrace to a threefold corner site on the lower terrace over a twofold coordinated site and therefore again only breaks one bond. It seems most likely that direct evaporation of step edge Ni atoms (mostly sevenfold coordinated) directly onto lower terraces through twofold coordinated bridge sites dominates the rate of annealing as the process requires breaking five bonds and thus costs roughly 0.9 eV/atom.

Such a proposition is also consistent with the decay rate being proportional to the density of the step edge atoms $\Delta\theta_{\text{edge}}$.

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