

## Rapid Communications

The Rapid Communications section is intended for the accelerated publication of important new results. Since manuscripts submitted to this section are given priority treatment both in the editorial office and in production, authors should explain in their submittal letter why the work justifies this special handling. A Rapid Communication should be no longer than 3½ printed pages and must be accompanied by an abstract. Page proofs are sent to authors, but, because of the accelerated schedule, publication is not delayed for receipt of corrections unless requested by the author or noted by the editor.

## Intensity oscillations for electron beams reflected during epitaxial growth of metals

S. T. Purcell, B. Heinrich, and A. S. Arrott

Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada V5A1S6

(Received 4 September 1986; revised manuscript received 27 January 1987)

Beam intensities in reflection high-energy electron diffraction (RHEED) are observed to oscillate during the epitaxial growth at 300 K of body-centered-cubic nickel on the (100) surface of iron and of face-centered-cubic Ni on the (100) surface of Ni. Such oscillations have been studied thoroughly by others for the growth of GaAs by molecular-beam epitaxy, where there is little doubt about the mechanisms of layer-by-layer growth. Because the RHEED oscillations are observed on vicinal surfaces [e.g., the (100) planes of the iron substrate are misoriented with respect to the surface by  $\sim 30$  mrad], the implication is that diffusion of Ni is sufficiently slow that growth does not take place by growing from the step edges, yet fast enough for completion of one monolayer before substantial development of the next. The demonstrated utility of RHEED oscillations for monitoring and controlling growth in GaAs is now applicable to metal growth.

It is well established<sup>1-3</sup> that observations of the intensity of reflection high-energy electron diffraction (RHEED) patterns, are useful for characterizing the epitaxial growth of GaAs by molecular-beam epitaxy (MBE). RHEED oscillations can be used to determine the completion of individual monolayers. They are particularly useful for the control of growth. We report here that RHEED oscillations can be exploited during MBE growth of metals on metal substrates, thus extending the technique to an area of metal physics of much current interest.

We have observed RHEED oscillations in the growth of fcc Ni on Ni(100) and bcc Ni on Fe(100). The periods of these oscillations are matched to the time for the deposition of one monolayer (within the limited accuracy of the mass determination,  $\sim 5\%$ ). This indicates both that the RHEED oscillations can be used to control growth and that the growths observed are essentially what is commonly termed layer by layer. It seems reasonable to project that RHEED oscillations will be seen in the growth of many metals if grown in a suitable temperature range. The purpose of this Rapid Communication is to call attention to the possibilities for the application of this powerful, yet simple, technique for the monitoring and control of metallic growth.

Though we have seen variations in the intensity of RHEED patterns during our various studies<sup>4,5</sup> of the epitaxial growth of metals on metal substrates by MBE, it was only with our current study<sup>6</sup> of the growth of bcc Ni on the (100) surface of iron at 300 K that we instrumented the intensity measurement by focusing the light from the RHEED screen onto a photomultiplier tube. The time

dependence of the RHEED intensity for bcc Ni on Fe(100) at 300 K is shown in Fig. 1. The oscillations persist beyond the sixth monolayer, but in the experiment illustrated they are obscured by a change in the level of the RHEED intensity which coincides with a change in the structure of the crystal surface. In this and some other

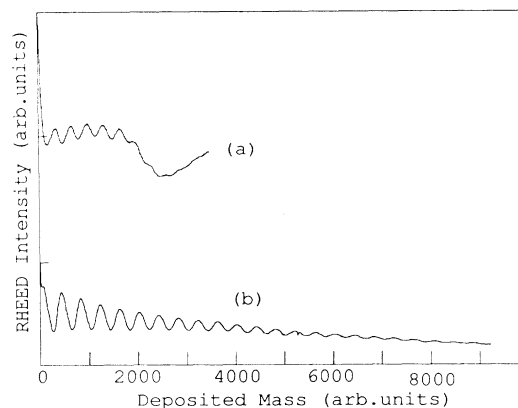


FIG. 1. Time dependence of the intensity of RHEED during the growth of (a) bcc Ni overlayers on Fe(100) and (b) fcc Ni overlayers on Ni(100). The position recorded is the intense area of the main RHEED streak for the starting substrate. The incoming beam is approximately down the steps of the vicinal surfaces. The slight variations in deposition rate during growth are taken into account by using the variable mass (arbitrary units, as measured by the integration of the Ni signal in the residual gas analyzer) in place of time.

runs the bcc streaks are augmented by some superlattice streaks<sup>6,7</sup> after the sixth monolayer (ML).

The temperature dependence of RHEED oscillations was not pursued with the bcc Ni on Fe(100) because these elements have a strong tendency to mix at temperatures above 500 K. Instead we investigated fcc Ni deposited on Ni(100) with the results shown in Fig. 1. The intensities for 300, 380, and 480 K show the disappearance of the oscillations with increase in temperature as found also for GaAs.

The iron crystal, grown by Takeuchi and Ikeda<sup>8</sup> using the strain and anneal technique, has its (001) axis misoriented with respect to the normal to the flat face by  $\sim 30$  mrad. In crystal-growth nomenclature, a surface with such a misorientation is called vicinal. The final polish is carried out using a commercial technique developed for polishing Si. NALCO 2350 is a colloidal silica slurry, 50- to 70-nm particles, produced by Rodel Products. It is applied using their Suba IV pads.

Once in the MBE facility, the Fe is sputtered using argon at 2 keV for 20 min at full raster ( $\sim 8 \mu\text{A}$  spread over  $1 \text{ cm}^2$ ). An initial treatment at  $600^\circ\text{C}$  produces high contrast, sharp RHEED patterns with strong Kikuchi lines, but brings sulfur to the surface. A repeat of the above sputtering process removes the sulfur. The second recrystallization of the Fe surface is carried out at  $500^\circ\text{C}$  for  $\sim 10$  min. The substrate is returned to 300 K for growth. The RHEED patterns are not quite as sharp. Some surface reconstruction is visible (see Fig. 1 of Ref. 5), the intensity of which is less than 5% of a principal bcc line.

The Ni single-crystal substrate was a disc cut from a boule at an angle of  $\sim 7$  mrad with respect to the (100) plane. The sample was polished to  $3\text{-}\mu\text{m}$  diamond on felt and then electropolished with a solution of 3:1 sulfuric acid in distilled water. The sputtering and annealing were carried out as for Fe. In each case Ni is evaporated from wire wrapped around a W filament. The growth rate is  $\sim 0.7$  ML/min.

In RHEED the electron beam strikes the surface at a small angle, typically 20–40 mrad. In the work reported here the intensity of the reflected beam close to the specular direction was monitored. Light, emitted when the diffracted electrons hit the phosphorescent RHEED screen, is focused onto a slit in front of a photomultiplier tube in order to monitor the RHEED intensity. The RHEED pattern has streaks in the direction perpendicular to the sample. These are separated on the screen by a distance inversely proportional to the atomic periodicity in the surface layer. There is structure both along and across the streaks. The slit is sufficiently wide as to integrate over the structure across the streaks (due to the steps in the vicinal surface), and sufficiently short in its long direction to look only at a region of an intensity maximum for the pattern from the substrate. Our PHI 400 MBE facility and its RHEED capability are essentially the same as described in the work of Cohen and collaborators.<sup>9</sup>

The Fe substrate was oriented in a [11] direction with the beam running approximately down the steps of the vicinal surface. For the Ni substrate we did not keep track of the orientation of the steps with respect to the measuring direction, but from the nature of the RHEED pattern,

we deduce that, again, the beam was coming in down the steps.

The origin of RHEED oscillations is in the differences in diffraction properties of a uniform surface and one which is populated by monolayer islands. One mechanism<sup>1,9</sup> is the interference in the diffraction between electron waves reflected from the growing layer (overlayer) and those reflected from the layer upon which the growth takes place. The argument can also be made<sup>2,10</sup> in terms of the density of edges being a maximum in a half-filled layer and a minimum for filled layers: This argument involves dynamical theory for the way the RHEED intensity depends upon whether the electrons leave at edges or through a smooth layer.<sup>11</sup> The latter argument leads one to expect oscillations in most any measurement of the surface. Indeed we observe oscillations in the intensities of Auger electron spectroscopy and x-ray photoelectron spectroscopy, by interrupting the growth for each measurement. In these cases the oscillations are not so obvious as they are superimposed on monotonically increasing or decreasing signals.<sup>6</sup>

In either case the reasoning is that whatever the condition of the surface is at time  $t=0$ , then at time  $t=\tau/2$ , where  $\tau$  is the time for the deposition of 1 ML, one-half of the sites are covered in layer-by-layer growth. This is a new condition of the surface, generally, but not always, distinguishable from the initial condition by the intensity of the RHEED pattern. (The exception could occur if a stepped surface were to grow by uniform propagation of each layer from the ledges, maintaining the same surface configuration, only translated. This might be the case at elevated temperatures where the atoms migrate to the ledges rather than forming monolayer islands away from the edges.) If initially the intensity is a maximum for the position observed, the intensity should decrease during the deposition of the first half ML. If at  $t=\tau$  the surface has been covered uniformly with 1 ML, the initial condition is recovered, and so should be the RHEED intensity. For oscillations to occur it is sufficient that something close to the initial condition is recovered at each  $t=n\tau$ . The extent to which the initial condition is not recovered contributes to the damping of the oscillations. If growth proceeds with atoms sticking close to where they hit, the development of upper layers on top of each overlayer before completion of the overlayer is sufficient to fully damp out the oscillations. (This may or may not happen at lower temperatures.)

A certain mobility of the added atoms is needed to insure completion of one layer before substantial growth of the upper layers. How much depends on the details of the growth. In the case of vicinal surfaces of GaAs, RHEED oscillations have been studied by Cohen and co-workers<sup>9</sup> and by Neave, Dobson, Joyce, and Zhang.<sup>10</sup> The latter attribute the appearance of the oscillations on stepped surfaces to a limited diffusion rate, where the atoms do not have enough time to migrate to the step edges. They observe that the oscillations, well developed at  $540^\circ\text{C}$ , become weaker and disappear as  $590^\circ\text{C}$  is approached, supporting their argument that limited diffusion is necessary for the appearance of RHEED oscillations.

For bcc Ni on Fe(100) and fcc Ni on Ni(100) the absolute temperature of growth is a factor of 3 lower than for

GaAs. It is likely that the mechanisms for monatomic growth of metals differ from the mechanism in GaAs growth. The perfection of the substrates is much poorer than for GaAs. Yet the general argument of Neave, Joyce, Dobson, and Norton<sup>2</sup> should still apply. One needs enough diffusion to permit completion of one layer before substantial development of the next layer, but not so much diffusion as to lead to the steps uniformly marching across the crystal. This condition seems to be fulfilled at 300 K for bcc Ni on Fe(100) and fcc Ni on Ni(100). The conditions for RHEED oscillations may not coincide with those for the best growths. It may be that RHEED oscillations in metals have not been previously observed because of the tendency to grow at somewhat higher temperatures where the RHEED patterns tend to remain sharper.

Clearly one can learn much by varying the conditions within the ranges for which RHEED oscillations can be observed during growth. For example, one can vary the

profile of deposition rate with respect to time to study time effects in surface atom diffusion.

The difference in the period of oscillation for Ni on Fe and Ni on Ni for the same rate of deposition is consistent with the 2:3 ratio in the density of atoms in a single layer of bcc Ni (the square lattice is 2.866 Å on a side) and fcc Ni (the square lattice is  $3.523/\sqrt{2}=2.49$  Å on a side). (The nearest-neighbor distances are essentially the same in the two lattices, but for the bcc lattice the nearest neighbor is in the next layer but not in the growth layer.)

We acknowledge the contributions to our continuing program on transition metals deposited on other transition metals by our co-workers C. Belanger, K. Mrytle, and K. B. Urquhart. The suggestion that we should measure RHEED oscillations came from Professor P. I. Cohen, who also provided information on the properties of our RHEED equipment.

<sup>1</sup>J. M. Van Hove, C. S. Lent, P. R. Pukite, and P. I. Cohen, *J. Vac. Sci. Technol. B* **1**, 741 (1983).

<sup>2</sup>J. H. Neave, B. A. Joyce, P. J. Dobson, and N. Norton, *Appl. Phys. A* **31**, 1 (1983).

<sup>3</sup>S. V. Ghaisas and A. Madhukar, *J. Vac. Sci. Technol. B* **3**, 540 (1985).

<sup>4</sup>B. Heinrich, C. Liu, and A. S. Arrott, *J. Vac. Sci. Technol. B* **3**, 766 (1985).

<sup>5</sup>B. Heinrich, A. S. Arrott, J. F. Cochran, C. Liu, and K. Mrytle, *J. Vac. Sci. Technol. A* **4**, 1376 (1986).

<sup>6</sup>B. Heinrich, A. S. Arrott, J. F. Cochran, S. T. Purcell, K. B. Urquhart, and K. Mrytle, *J. Cryst. Growth* (to be published). See also, B. Heinrich, A. S. Arrott, J. F. Cochran, S. T. Purcell, K. B. Urquhart, N. Alberding, and C. Liu, in *Thin Film Growth Techniques for Low Dimensional Structures*, edited by R. F. C. Farrow (Plenum, New York, 1987).

<sup>7</sup>Z. Q. Wang, Y. S. Li, and F. Jona (unpublished). Their LEED

work confirms our original contention (Ref. 5) that bcc Ni grows epitaxially on Fe(100). After six layers they report the appearance of a  $c 2 \times 2$  pattern. Some of our growths are consistent with their observations.

<sup>8</sup>T. Takeuchi and S. Ikeda, *Trans. Iron Steel Inst. Jpn.* **9**, 484 (1969).

<sup>9</sup>J. M. Van Hove, P. R. Pukite, and P. I. Cohen, *J. Vac. Sci. Technol. B* **3**, 563 (1985); P. R. Pukite, C. S. Lent, and P. I. Cohen, *Surf. Sci.* **161**, 39 (1985); P. R. Pukite, J. M. Van Hove, and P. I. Cohen, *J. Vac. Sci. Technol. B* **2**, 456 (1984); C. S. Lent and P. I. Cohen, *Phys. Rev. B* **33**, 8329 (1986).

<sup>10</sup>J. H. Neave, P. J. Dobson, B. A. Joyce, and Jing Zhang, *Appl. Phys. Lett.* **47**, 100 (1985); B. A. Joyce, P. J. Dobson, J. H. Neave, K. Woodbridge, J. Zhang, P. K. Larsen, and B. Bölger, *Surf. Sci.* **168**, 423 (1986).

<sup>11</sup>T. Kawamura and P. A. Maksym, *Surf. Sci.* **161**, 12 (1985).