

# Growth of fcc Fe films on diamond

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The epitaxial growth of fcc iron films on the (001) face of diamond has been achieved. The films were studied by reflection high-energy electron diffraction and angle-resolved Auger electron diffraction. The studies show that 4–5 atomic layers of Fe on C(100) form a continuous film. The films as deposited at room temperature are disordered, and after a high-temperature anneal have a fcc structure at room temperature.

Epitaxial growth of various stable and metastable phases of matter on lattice-matched substrates has opened an entirely new field of experimental and theoretical physics.<sup>1</sup> In this paper we report an important addition to the field of the growth of metastable phases of elemental transition metals via epitaxy, namely, the growth of Fe on the (001) face of diamond.

Of the 3d transition metals, Fe provides the most varied family of crystallographic phases. At low temperatures, Fe is stable in a ferromagnetic bcc phase ( $\alpha$ -Fe), while at 1184 K it converts to an antiferromagnetic fcc phase ( $\gamma$ -Fe) with a lattice constant of  $a=3.6468$  Å. Above 1664 K, it then reverts back to a bcc structure, which is paramagnetic. Extrapolation of the fcc Fe lattice constant down to room temperature gives  $a\approx 3.59$  Å, and it is well known that fcc Fe can be stabilized on Cu substrates<sup>2–4</sup> which have fcc lattices with  $a=3.6147$  Å. The metastable fcc-Fe/Cu structure has attracted much interest lately from the magnetism community since it has been observed that under low-temperature (100–300 K) growth conditions, thin films of fcc-Fe/Cu(001) are ferromagnetic with a strong perpendicular anisotropy.<sup>5</sup>

The epitaxial growth of fcc transition metals on diamond is feasible due to the close lattice match ( $a=3.5668$  Å for diamond), so the (001) surface net of the diamond and fcc lattices match very closely. The use of diamond substrates for such growth is appealing due to the unusual properties of diamond, i.e., its large band gap, high thermal conductivity, extreme hardness, and desirable optical properties. The characterization and optimization of the interfacial properties between diamond and various metals is a necessary step in the development of diamond-based electronic devices. An understanding of the structural and magnetic properties of transition-metal films on diamond may also provide a means of developing diamond-based, nonvolatile magnetic storage devices.

Recent work by Humphreys *et al.*<sup>6</sup> has shown that it is possible to grow continuous, single-crystal films of fcc Ni(001) on C(001) by electron-beam epitaxy. It might also be expected that fcc Fe can be stabilized on C(001). In earlier work<sup>7</sup> we have shown that the reflection high-energy electron diffraction (RHEED) patterns of such Fe films have the expected symmetry for fcc growth which is oriented by the C(001) substrate. It was also shown with RHEED and extended x-ray absorption fine-structure (EXAFS) techniques that subsequent Cu films grown on this Fe seed are oriented to the substrate in an fcc structure. The RHEED from thin Cu

overlayers (thickness  $<300$  Å) shows evidence of a surface reconstruction and the quality of the RHEED patterns from very thick (1350 Å) Cu/Fe/C(001) structures are comparable to that of a single-crystal Cu standard. The EXAFS study of the 1350-Å Cu/Fe/C(001) structure revealed an fcc structure with a slight tetragonal distortion. However, the fcc structure of the Fe seed could not be confirmed by EXAFS because of the low sample volume of Fe and the strong attenuation of the Fe EXAFS signal by the Cu overlayer. In the present study we examine Fe/C(001) *in situ* using angle-resolved Auger electron diffraction (AED) and compare the resulting line scans to experimental standards of fcc and bcc structures. This comparison shows that the Fe has an fcc structure.

The  $3\times 3\times 2$ -mm<sup>3</sup> C(001) substrates used in this work were cleaned by etching in an *aqua regia* solution and then boiling in an H<sub>2</sub>O<sub>2</sub>-NH<sub>4</sub>OH-H<sub>2</sub>O solution followed by a rinse in deionized water. The substrate was then loaded into a UHV chamber (base pressure  $<1\times 10^{-10}$  Torr) and the surface was characterized using the RHEED method. Electrical contact was made with the surface in order to reduce charging effects which are characteristic of these substrates under electron-beam bombardment.

The Fe was deposited by sublimation from an electron-beam-heated rod while the pressure stayed below  $5\times 10^{-10}$  Torr. For the results shown in this paper, the film thickness was  $8\pm 2$  Å, as measured with a quartz-crystal monitor. In our studies we find that the results shown herein are typical for films in the thickness range of approximately 5 to 15 Å. During the Fe growth the C(001) substrate was left at room temperature. After 5 Å of Fe had been deposited there was a complete loss of the C(001) RHEED pattern and only a bright diffuse background with a weak specular reflection was observed. This suggests that the Fe has covered the diamond in a continuous film. We also note that at room temperature the Fe AES uptake curve follows a smooth exponential increase up to at least 20 Å. A fit of the normalized Fe Auger signal [i.e., Fe:(Fe+C), using the 703- and 273-eV Auger transitions for Fe and C, respectively] saturates to 1 with an attenuation constant 10 Å, which again is consistent with a continuous Fe coverage. By comparison, the normalized Fe uptake curve taken with the substrate held at 300 °C during deposition saturates at 0.6, and evidence of the sharp C(001) RHEED pattern is still evident up to 20 Å coverage. These effects are characteristic of the Fe agglomerating into islands and possibly carbon diffusing into the Fe under high-temperature growth conditions.

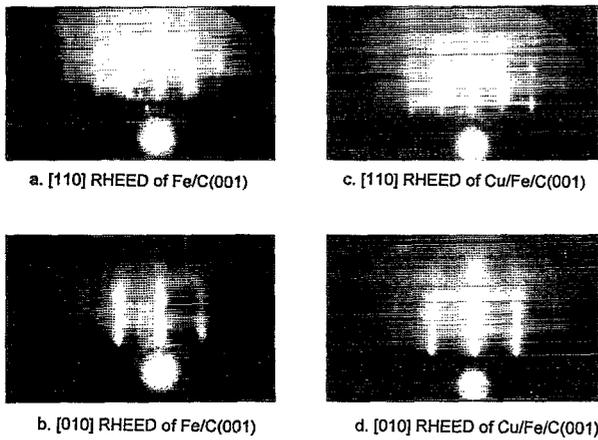


FIG. 1. RHEED patterns from the high-symmetry directions for 8-Å Fe/C(001) which has been annealed to  $\approx 500$ – $600$  °C and 150-Å Cu grown on Fe/C(001) at room temperature.

Clearly, it is possible to obtain a disordered, continuous Fe film on diamond by deposition at room temperature. The room-temperature-grown film was then annealed while the RHEED pattern was monitored. As discussed in Ref. 7, after an anneal to 350 °C a weak RHEED pattern with the correct symmetry for a (001) cubic surface was first evident, and there was no change in the C:Fe AES intensities. A slight increase in the C:Fe AES intensity ratio is observed upon further annealing of the Fe film to 500–600 °C, which results in the RHEED patterns for the [110] and [010] directions as shown in Figs. 1(a) and 1(b), respectively. There is no evidence of the C(001) RHEED pattern after the high-temperature anneal, and we conclude that the increase in the C:Fe AES intensity may be due to some carbon diffusing through the Fe from the substrate. In addition, we note that after the anneal there was no evidence of oxygen or other contamination on the Fe surface as evaluated by an AES energy scan, and in fact the anneal to high temperature removes oxygen contamination (which accumulates onto the film after growth) from the surface.

The patterns shown in Figs. 1(a) and 1(b) match closely those taken from the fcc Cu RHEED patterns discussed in the previous study<sup>7</sup> and are typical of a (001) cubic face which is oriented in registry with the C(100) substrate. For comparison, the RHEED patterns from a 100-Å fcc Cu film are shown in Figs. 1(c) and 1(d). The most striking feature in the [110] RHEED patterns is the appearance of extra spots along diagonal lines between the main intensity maxima. These spots are evident in both the Fe and Cu RHEED patterns and may be indicative of faceting of the diamond substrate or long-range reconstructions on the Fe and Cu surfaces. The [010] Fe RHEED pattern shows a clear second-order reconstruction streak which is absent in the Cu RHEED pattern, showing that there is a surface reconstruction of the Fe film which doubles the unit cell in the [100] direction.

In order to determine the local symmetry of the Fe lattice, Auger electron diffraction<sup>8–10</sup> (AED) on the Fe 703-eV LVV Auger transition has been conducted. The details of the apparatus and data collection are given in Ref. 11. In the

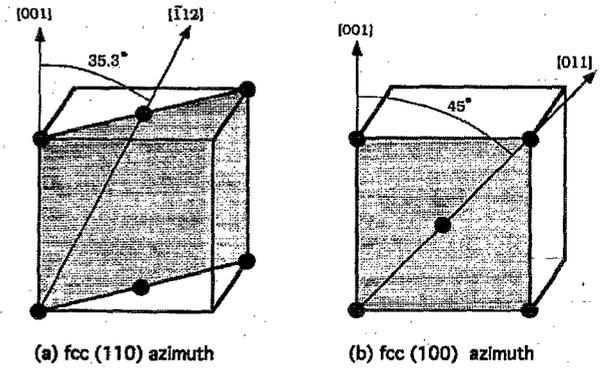


FIG. 2. Schematic of the planes in which the polar scans of the AED is taken. All angles are measured with respect to the surface normal, i.e., the [001] direction. The directions of prominent forward focusing maxima which are observed from fcc lattices are illustrated.

present study, the Fe Auger intensity from the (001) face is measured as a function of polar angle for low-symmetry azimuths and compared to polar scans from fcc Cu(001) and bcc Fe(001) experimental standards: all polar angles are given with reference to the [001] direction. A picture of the (110) and (100) fcc azimuths are shown in Figs. 2(a) and 2(b) for reference. For emission along chains of atoms, e.g., at 35.3° and 45° in Figs. 2(a) and 2(b), respectively, the Auger intensity can be either enhanced or suppressed, depending on the energy and final state of the emitted electron.<sup>12,13</sup> At the intermediate energies of the Fe and Cu LVV Auger electrons, it is generally accepted that constructive self-interference of the Auger electrons along the chain direction is seen. This is also referred to as the forward focusing effect. In addition, higher-order diffraction peaks which are specific to the local environment of the atoms will be seen at intermediate angles.<sup>8</sup>

In Fig. 3, polar scans of the AED signal from 8 Å of Fe/C(001) are shown for the (110) and (100) azimuths. Experimental standard spectra from a bulk fcc Cu crystal and a thick bcc Fe film grown on GaAs are also shown just above and below the test spectrum for comparison. The standard spectra were obtained using the Cu 920-eV and Fe 703-eV Auger transitions. It is clear that the angular line scans from

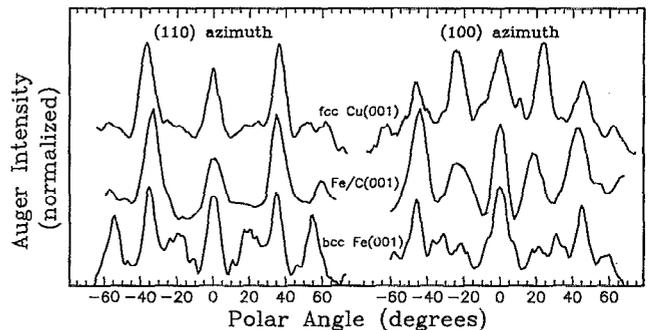


FIG. 3. Polar scans of the angle-resolved Auger intensity from 8-Å Fe/C(001) which has been annealed (middle), and bulk fcc Cu(001) and bcc Fe(001) experimental standards (top and bottom, respectively).

the Fe/C(001) match to the fcc standard much better than to the bcc standard in both azimuths. In particular, for the (110) azimuth a bcc structure has a strong peak at  $54.7^\circ$  (i.e., along the body diagonal). This peak is clearly absent in the Fe/C(001) line scan, while the weak higher-order diffraction peaks shown by the fcc standard between  $50^\circ$  and  $60^\circ$  are reproduced in the Fe/C(001) structure. The higher-order bcc diffraction peaks between  $15^\circ$  and  $30^\circ$  are also missing for the Fe/C(001) structure, which again matches closely the fcc standard.

Comparison of the (100) azimuth polar scans shows that the diffraction effects between  $15^\circ$  and  $40^\circ$  in the Fe/C(001) structure match much closer to the fcc standard than the bcc. The main difference between the Fe/C(001) and fcc Cu(001) and (100) azimuth polar scans is the increased ratio between the  $45^\circ$  peak and the low angle ( $20^\circ$ – $25^\circ$ ) peak. However, this ratio is known to decrease as the electron energy is tuned from 900 to 700 eV,<sup>14</sup> as is the case for the Cu and Fe Auger lines used in the present study. This effect is less pronounced in the (110) azimuth, which accounts for the good agreement found in that case.

A second aspect of Fig. 3 is the systematic shift of the Fe/C(001) AED peaks to slightly lower angles than in the standards. This effect is seen consistently in the Fe/C(001) AED curves, and can be modeled with an  $\approx 3\%$  expansion of the fcc Fe lattice perpendicular to the plane of the film. A similar expansion has been observed for fcc-Fe/Cu(001).<sup>4</sup> This deformation of the lattice is most likely a manifestation of the stress involved in stabilizing the fcc phase of Fe at room temperature and the fact that the in-plane surface net is subject to an  $\approx 1\%$  compression. This strain may also drive the reconstructions seen in the Fe RHEED patterns, which are similar to the reconstructions seen in low-energy electron diffraction patterns from fcc-Fe/Cu(001).<sup>15</sup>

We have shown in this study that thin fcc-Fe films can be stabilized on the (001) face of diamond. Both the RHEED

and AED show that the Fe film is oriented with respect to the crystalline axes of the substrate; however, evidence of strain is seen using both techniques. A possible utilization of such a film is as a seed for the metallization of the surface with Cu, as shown here and in Ref. 7. The data shown in Ref. 7 are also consistent with fcc-Fe/C(001) being ferromagnetic, which opens this system to possible applications for magnetic storage and sensor technology as well. These studies show that the structural and magnetic phases of Fe merit further study, and that diamond can be used as a suitable substrate for the growth of transition-metal structures.

- <sup>1</sup>L. M. Falicov, D. T. Pierce, S. D. Bader, R. Gronsky, K. B. Hathaway, H. Hopster, D. N. Lambeth, S. S. P. Parkin, G. Prinz, M. Salamon, I. K. Schuller, and R. H. Victora, *J. Mater. Res.* **5**, 1299 (1990).
- <sup>2</sup>S. H. Lu, J. Quinn, D. Tian, F. Jona, and P. M. Marcus, *Surf. Sci.* **209**, 364 (1989).
- <sup>3</sup>A. Clarke, P. J. Rous, M. Arnott, G. Jennings, and R. F. Willis, *Surf. Sci.* **192**, L843 (1987).
- <sup>4</sup>Y. Darici, J. Marcano, H. Min, and P. A. Montano, *Surf. Sci.* **217**, 521 (1989).
- <sup>5</sup>C. Liu, E. R. Moog, and S. D. Bader, *Phys. Rev. Lett.* **60**, 2422 (1988).
- <sup>6</sup>T. P. Humphreys, H. Jeon, R. J. Nemanich, J. B. Posthill, R. A. Rudder, D. P. Malta, G. C. Hudson, R. J. Markunas, J. D. Hunn, and N. R. Parikh, *Mater. Res. Soc. Symp. Proc.* **202**, 463 (1991).
- <sup>7</sup>D. P. Pappas, J. W. Glesener, V. G. Harris, J. J. Krebs, Y. U. Idzerda, A. A. Morrish, and G. A. Prinz, *Mater. Res. Soc. Proc.* (to be published).
- <sup>8</sup>S. A. Chambers, *Surf. Sci. Rep.* **16**, 261 (1992).
- <sup>9</sup>C. S. Fadley, *Prog. Surf. Sci.* **16**, 275 (1984); in *Synchrotron Radiation Research: Advances in Surface Science*, edited by R. Z. Bachrach (Plenum, New York, 1990).
- <sup>10</sup>W. F. Egelhoff, Jr., *Crit. Rev. Solid State Mater. Sci.* **16**, 213 (1990).
- <sup>11</sup>Y. U. Idzerda and G. A. Prinz, *Phys. Rev. B* **43**, 11460 (1991).
- <sup>12</sup>Y. U. Idzerda and D. E. Ramaker, *Phys. Rev. Lett.* **69**, 1943 (1992).
- <sup>13</sup>T. Greber, J. Osterwalder, D. Naumović, A. Stuck, S. Hüfner, and L. Schlapbach, *Phys. Rev. Lett.* **69**, 1947 (1992).
- <sup>14</sup>Z.-L. Han, S. Hardcastle, G. R. Harp, H. Li, X.-D. Wang, J. Zhang, and B. Tonner, *Surf. Sci.* **258**, 313 (1991).
- <sup>15</sup>W. Daum, C. Stuhlman, and H. Ibach, *Phys. Rev. Lett.* **60**, 2741 (1988).