PHYSICAL REVIEW B VOLUME 51, NUMBER 15 15 APRIL 1995-I

Unusual island structures in Ag growth on Si(100)-(2×1)

N. Doraiswamy, G. Jayaram, and L. D. Marks
Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208

(Received 30 December 1994)

A detailed study of the early stages of nucleation and growth of Ag on Si(100)-(2×1) surfaces at room temperature using ultrahigh-vacuum high-resolution transmission-electron-microscopy imaging and diffraction is presented. While diffraction patterns suggest only a mixed epitaxy, off-zone axis images clearly reveal three-dimensional Ag islands. Aside from simple single-crystal structures, these islands are also seen to include multiply twinned morphologies with different epitaxies relative to the substrate; details of these are discussed.

The early stages of nucleation and growth play a crucial role in determining the final structure, and therefore the properties, of epitaxial deposits. It is well known that nucleation during crystal growth typically proceeds via one of the following three routes: layer by layer (Frank–van der Merwe), three-dimensional (3D) islands (Volmer-Weber), or layer plus island (Stranski-Krastanov). In the latter two cases, further growth of the 3D islands occurs by enlargement of preexisting nuclei and/or coalescence of neighboring islands. During these processes, the islands can either retain their original structures or undergo recrystallization to form new structures. The role of the island structure is thus critical in controlling the properties of many heteroepitaxial systems, and an understanding of their initial structure is therefore highly desirable.

The Ag/Si(100) system is governed by island nucleation and growth,[1–16] and is of interest primarily from a technological standpoint: the Ag/Si interface is atomically abrupt and is therefore used as a model system to study Schottky-barrier heights as a function of interfacial microstructure. However, despite its importance, the Ag/Si(100) system has received relatively little attention. The nucleation and growth mode of Ag both at the initial stages and for thicker films has been characterized as Stranski-Krastanov from scanning-tunneling microscopy (STM),[1–7] low energy electron diffraction Auger-electron spectroscopy (LEED-AES),[8–12] surface reflection spectroscopy–Auger electron spectroscopy (SRS-AES),[13] and reflection high-energy electron-diffraction (RHEED) (Refs. 14 and 15) investigations; further, Ag is reported to grow with different epitaxies, i.e., $\langle 100\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$ of Ag normal to the Si(100) surface. Surprisingly, little is actually known about the structure of the 3D islands: while the external morphology is assumed to be flat with mostly $\{111\}$ and $\{100\}$ facets,[4,12,13,15] only two investigations[16,17] have even alluded to the internal structure within the islands; most studies assume a simple single-crystal structure.

This paper reports a detailed study of the structure of 3D islands that nucleate during the early stages of growth of Ag on Si(100)-(2×1) surfaces at room temperature using a combination of ultrahigh-vacuum high-resolution transmission-electron-microscopy imaging (UHV-HREM) and diffraction (TED) techniques. Contrary to earlier suppositions, the Ag islands are seen to be a mixture of single-crystal and multiply twinned particle (MTP)[18] morphologies. While the observation of mixed morphologies is in good agreement with similar studies on carbon, SiO, and LiF (Ref. 19) substrates, the dominance of the decahedral type (Dh) over the icosahedral type (Ic) MTP's contradicts all earlier experimental and theoretical studies.

Thin samples of *p*-type Si(100) (B doped at 1 Ω cm) were mechanically polished, slightly dimpled, and chemically thinned in a 10% HF + 90% HNO_3 solution before being transferred into a UHV surface science chamber (UHV-SSC) attached to a Hitachi UHV-H9000 electron microscope[20] (which was operated at 300 and 250 kV, the latter to minimize radiation damage) with a working vacuum of 7×10^{-11} torr. *In situ* sample preparation involved a cyclic combination of 2.5-kV Ar^+ sputtering and electron-beam annealing cycles, and clean surfaces were characterized by the appearance of the (2×1)-type surface spots. The Ag evaporator filaments were carefully outgassed, and several monolayers of Ag were then deposited onto clean Si(100) surfaces at room temperature inside the UHV-SSC. Following each observation, the sample was ion milled and annealed to establish the clean Si surface reconstruction before further deposition (sample cleanliness was carefully monitored after each deposition cycle using parallel electron-energy-loss spectroscopy). The results reported below are from numerous such observations.

Consistent with earlier diffraction studies,[8,9,14] TED patterns showed a decrease in the intensity of the Si surface reconstruction spots with increasing Ag coverage. Faint arcs whose spacings correspond to those of bulk Ag were also observed from the very initial stages suggestive of an abrupt Ag/Si interface. A typical TED pattern in Fig. 1 shows the coexistence of 2×1 spots of the clean substrate and (111) and (220) arcs of Ag. These can be indexed in terms of a primary $\langle 110\rangle$ epitaxy (i.e., normal to the surface) with some rotational disorder and strain, moiré fringes between the particles and substrate, and moiré fringes internal to the particles themselves;[18,21] we

0163-1829/95/51(15)/10167(4)/$06.00

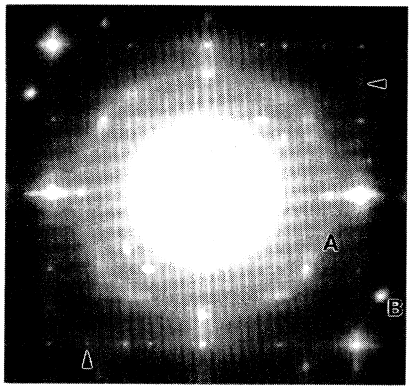

FIG. 1. A typical TED pattern following Ag deposition on a Si(100)-(2×1) surface; arrowed surface reconstruction spots coexist with the (111) and (220) rings of Ag, denoted by the letters *A* and *B*. All features can be interpreted by a combination of silicon, silver, and moiré spacings.

will clarify this below, but for the moment we should note that these diffraction patterns are actually highly misleading. With increasing coverages an increase in the intensities of these arcs was accompanied by the disappearance of the Si reconstruction spots (leaving behind the 1×1 Si lattice); at somewhat higher coverages a true polycrystalline ring pattern developed.

HREM images were acquired in both the on- and off-zone axis modes. Aside from dark contrast features of Ag with extensive moiré fringes, the on-zone axis images provided little information about the actual structure of the deposited layer due to the strong underlying bulk signal. In order to reduce the latter and understand better the structure of the features, the sample was tilted 2–3° off the (100) zone to obtain off-zone images. This technique is very sensitive to the substrate surface[22] or deposit overlayers, i.e., the Ag layer in our case, and revealed all information reported about their structure and nature in this paper. In order to further enhance the image contrast, a modified Wien filter[23] was applied to all HREM images (to reduce the shot noise in the image without introducing any artifacts). The images revealed the presence of 3D Ag islands (dark contrast features in the on-zone case); these islands have complicated structures and were analyzed using an image processing software, SEMPER. The presence of 3D islands from the very early stages of nucleation and growth agrees well with the predicted growth mode,[1–16] and details of their morphologies form the remainder of this paper.

Most particles were around 3-4 nm in size; an analysis of the internal particle morphologies revealed that about half of them were single crystals (Sc) with a primary ⟨100⟩ epitaxy and a smaller number in a ⟨110⟩ epitaxy [Fig. 2(a)]. The rest were comprised of particles that were internally twinned between the adjoining (111) faces, i.e., multiply twinned particles (MTP's).[18] The highest fraction of these particles were of the decahedral (Dc) type that had nucleated with a ⟨110⟩ epitaxy [see Fig. 2(b)], while a very small population (about 2% of the total) were seen to be of the icosahedral (Ic) type with a ⟨112⟩ orientation, as shown in Fig. 2(c) (for more details about the structure of these MTP's as observed by HREM, see Refs. 21, 24, and 25). It is the presence of these more complicated particles that cause both the arcs and the other additional spots in the diffraction patterns.[18]

Such mixed morphology growth is known to exist in fcc metal islands deposited on oxide and alkali halide substrates,[18,21,26–29] and were first observed only under very clean conditions.[18,30] Theoretical results[31–35] have also clearly demonstrated that MTP's are thermodynamically stable entities at the small sizes seen in this investigation; similar results in terms of relative probabilities of oc-

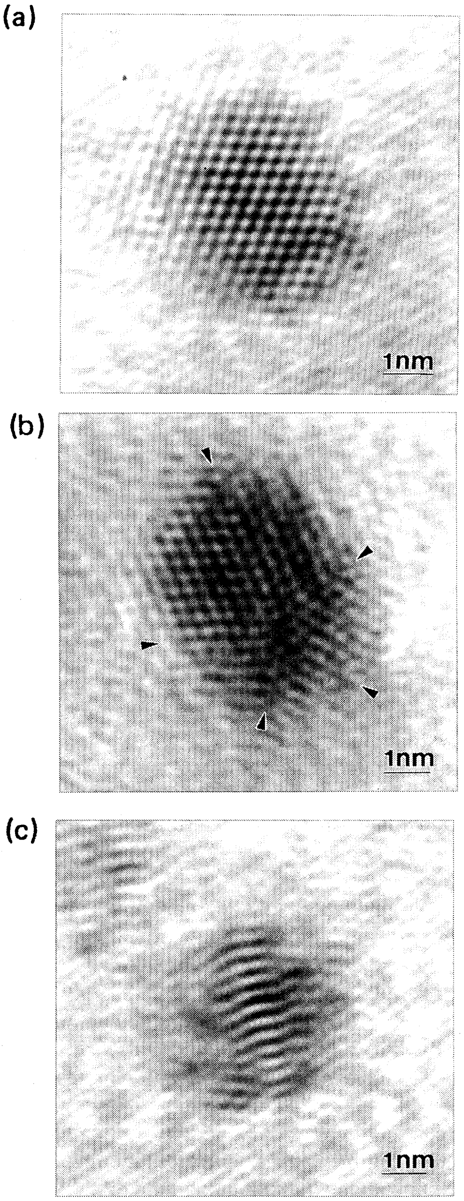

FIG. 2. UHV-HREM micrographs of the different 3D Ag island morphologies on clean Si(100) surfaces. (a) A ⟨110⟩-oriented single crystal; the cross fringes in the single-crystal image are due to the (111) planes. (b) A ⟨110⟩-oriented decahedral MTP with arrows indicating the five twins separating {111} facets. (c) A ⟨112⟩-oriented icosahedral MTP.

currence of Ic's, Dh's, and Sc's have been reported in a recent experimental study.[36]

In contrast to these studies, the Ag/Si(100) system behaves uniquely, i.e., although it is a mixed morphology system, there was an unusual lack of Ic particles. Without exception that we are aware of, Ic particles are considered to be energetically preferred over the Dc particles[31–35,37] at these small size ranges. All theoretical analyses to date (except the early work of Ino[31]) have ignored the substrate interaction effect. Since there is no simple way for an Ic particle to adopt an ⟨110⟩ epitaxy, we hypothesize that the deposit/substrate interaction effect (interface) inhibits their formation. The influence of the substrate on the particle morphologies was supported by the following observation: on exposure to air, although the Ag particles continued to exhibit a mixed morphology of single crystals and MTP's, the fraction of the Ic particles increased. This can be attributed to the effect of the gas environment on both the interface between Ag and Si and on the Ag surface free energy[32–33] (both its absolute value and anisotropy).

Although the morphologies reported in this study are of the static type (no fluctuations were observed under the beam fluxes used), there was evidence of interconversion during growth. One particularly striking example is the pentagonal-shaped single crystal shown in Fig. 3 (which was observed in UHV prior to the air transfer). A pentagonal shape is not close to any equilibrium shape for a Sc indicating that a Dc particle was transformed by grain-boundary migration[38] to a single crystal. Interconversion of particles has been relatively well documented[39–41] since the initial observations by Yagi *et al.*[39] during growth in UHV conditions.

The small fraction of Ic particles raises some fundamental scientific questions about the variation in types of island morphologies with environmental conditions, and merits further investigation. Further, the changes in the fraction of Ic particles on exposure to air underlines the importance of observation under UHV conditions. A subtle point that also arises is the advantage of UHV-HREM over STM as an imaging technique in resolving the local structure within these small 3D islands; the pitfall of an erroneous interpretation of the nucleation and growth mechanism based solely on diffraction data is also revealed.

The observations conclusively show that, rather than being simple flat single crystals (as suggested without proof in earlier studies), the 3D Ag islands show a classic mixed morphology MTP growth,[18] i.e., a combination of single crystals and multiply twinned particles with different orientations relative to the substrate (this is possibly the reason for the different epitaxies reported for this system by earlier studies). This could also be the case for the Ag/Si(111) system; we have also observed MTP's in the Au/Si(111) system.[42] The investigation thus demonstrates that one of the most fundamental questions about the growth mode of Ag on clean Si(100), i.e., the particle structure, has escaped more than a decade of study.

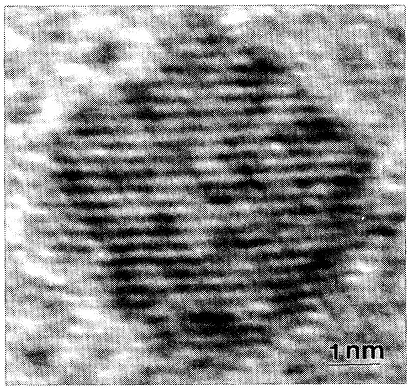

FIG. 3. An atypical pentagonal Ag single crystal on a Si(100)-(2×1) surface indicating intermorphology conversion via grain-boundary migration.

The formation of MTP's in the initial stages has profound implications on the later stages of growth. Earlier studies[43,44] have shown that these MTP's on coalescence can form single particles (with either the MTP/Sc structure), polyparticles (partially coalesced MTP's), or polycrystals (single crystals separated by a grain boundary); recrystallization is also seen to occur in these particles as a means of relieving the strain. The final film is a result of these processes; its structure will therefore be strongly dependent on the processing conditions (temperature, deposition rate, vacuum, etc.). A time-temperature-transformation morphology map similar to that suggested by Marks[41] would be essential in controlling the final structure and therefore the properties in such mixed morphology systems (e.g., the resulting film[45] would have a variation in Schottky-barrier height ranges depending on the inhomogenity and polycrystallinity developed during the process of growth).

---

[1] A. Samsavar, T. Miller, and T.-C. Chiang, Phys. Rev. B **38**, 9889 (1988).

[2] A. Samsavar *et al.*, Phys. Rev. Lett. **63**, 2830 (1989).

[3] T. Hashizume *et al.*, J. Vac. Sci. Technol. A **8**, 249 (1990).

[4] A. Brodde *et al.*, J. Vac. Sci. Technol. A **8**, 251 (1990).

[5] X. F. Lin, K. J. Wan, and J. Nogami, Phys. Rev. B **47**, 10 947 (1993).

[6] X. F. Lin, K. J. Wan, and J. Nogami, Phys. Rev. B **47**, 13 491 (1993).

[7] D. Winau *et al.*, Surf. Sci. **303**, 139 (1994).

[8] T. Hanawa and K. Oura, Jpn. J. Appl. Phys. **16**, 519 (1977).

[9] M. Hanbücken and H. Neddermeyer, Surf. Sci. **114**, 563 (1982).

[10] M. Hanbücken, H. Neddermeyer, and P. Rupieper, Thin Solid Films **90**, 37 (1982).

[11] M. Hanbücken, M. Futamoto, and J. A. Venables, Surf. Sci. **147**, 433 (1984).

[12] M. Hanbücken and G. LeLay, Surf. Sci. **168**, 122 (1986).

[13] Y. Borensztein and R. Alameh, Appl. Surf. Sci. **65/66**, 735 (1993).

[14] K. Nishimori *et al.*, Surf. Sci. **242**, 157 (1991).

[15] Y. Kimura and K. Takayanagi, Surf. Sci. **276**, 166 (1992).

[16] F. C. H. Luo, G. G. Hembree, and J. A. Venables, in *Proceedings of the Materials Research Society,* edited by C. V. Thompson, J. Y. Tsao, and D. J. Srolovitz (Materials Research Society, Pittsburgh, 1991), Vol. 202, p. 49.

[17] J. Shirokoff and U. Erb, Philos. Mag. Lett. **58**, 255 (1988).

[18] S. Ino, J. Phys. Soc. Jpn. **21**, 346 (1966).

[19] A. K. Green, J. Dancy, and E. Bauer, J. Vac. Sci. Technol. **7**, 159 (1969).

[20] J. E. Bonevich and L. D. Marks, Microscopy **22**, 95 (1992).

[21] L. D. Marks and D. J. Smith, J. Cryst. Growth **54**, 425 (1981).

[22] P. Xu *et al.*, Surf. Sci. Lett. **285**, L479 (1993).

[23] L. D. Marks (unpublished).

[24] P. A. Buffat *et al.*, Faraday Discuss. **92**, 173 (1991).

[25] A. I. Kirkland *et al.*, Proc. R. Soc. London Ser. A **34**, 279 (1991).

[26] M. Gillet, Surf. Sci. **67**, 139 (1977).

[27] A. Renou and A. Rudra, Surf. Sci. **156**, 69 (1985).

[28] C. Altenhein *et al.*, Z. Phys. D **19**, 303 (1991).

[29] H. Hofmeister, Z. Phys. D **19**, 307 (1991).

[30] J. G. Allpress and J. V. Sanders, Surf. Sci. **7**, 1 (1967).

[31] S. Ino, J. Phys. Soc. Jpn. **27**, 941 (1969).

[32] L. D. Marks, Philos. Mag. A **49**, 81 (1984).

[33] A. Howie and L. D. Marks, Philos. Mag. A **49**, 95 (1984).

[34] P. M. Ajayan and L. D. Marks, Phase Trans. **24**, 229 (1990).

[35] C. Cleveland and U. Landman, J. Chem. Phys. **94**, 7376 (1991).

[36] N. Doraiswamy and L. D. Marks, Philos. Mag. B **71**, 291 (1995).

[37] B. D. Hall *et al.*, Phys. Rev. B **43**, 3906 (1991).

[38] J. E. Bonevich and L. D. Marks, J. Mater. Res. **7**, 1489 (1992).

[39] K. Yagi *et al.*, J. Cryst. Growth **28**, 117 (1975).

[40] S. Iijima and T. Ichihashi, J. Appl. Phys. **24**, L125 (1985).

[41] L. D. Marks, Rep. Prog. Phys. **57**, 533 (1994).

[42] R. Plass (private communication).

[43] G. Honjo *et al.*, Phys. Status Solidi A **55**, 353 (1979).

[44] L. D. Marks, Thin Solid Films **136**, 309 (1986).

[45] H. H. Weitering *et al.*, Appl. Surf. Sci. **70/71**, 422 (1993).

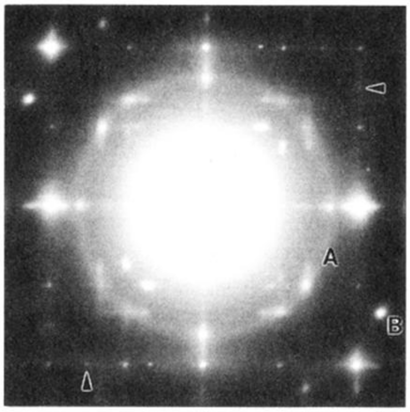

FIG. 1. A typical TED pattern following Ag deposition on a Si(100)-(2×1) surface; arrowed surface reconstruction spots coexist with the (111) and (220) rings of Ag, denoted by the letters *A* and *B*. All features can be interpreted by a combination of silicon, silver, and moiré spacings.

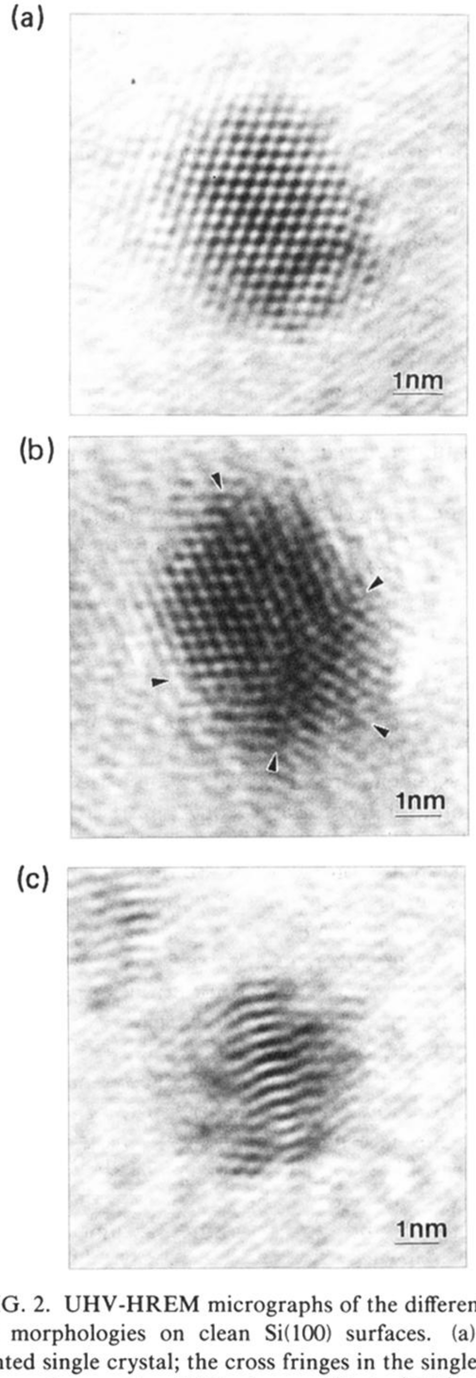

FIG. 2. UHV-HREM micrographs of the different 3D Ag island morphologies on clean Si(100) surfaces. (a) A ⟨110⟩-oriented single crystal; the cross fringes in the single-crystal image are due to the (111) planes. (b) A ⟨110⟩-oriented decahedral MTP with arrows indicating the five twins separating {111} facets. (c) A ⟨112⟩-oriented icosahedral MTP.

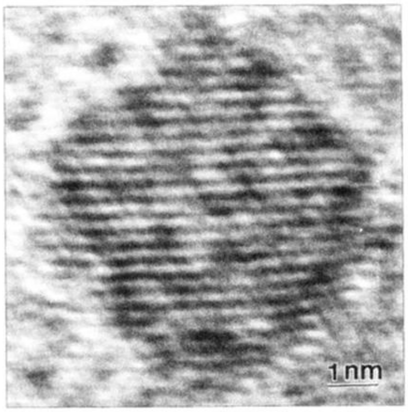

FIG. 3. An atypical pentagonal Ag single crystal on a Si(100)-(2×1) surface indicating intermorphology conversion via grain-boundary migration.