RESEARCH ARTICLE | JUNE 28 2004

Chemistry-mediated two-dimensional to three-dimensional transition of In thin films

H. L. Wei; Hanchen Huang; C. H. Woo; X. X. Zhang; L. G. Zhou

Appl. Phys. Lett. 84, 5401–5403 (2004)
https://doi.org/10.1063/1.1767595

APPLIED PHYSICS LETTERS VOLUME 84, NUMBER 26 28 JUNE 2004

Chemistry-mediated two-dimensional to three-dimensional transition of In thin films

H. L. Wei
Department of Electronic and Information Engineering, Hong Kong Polytechnic University, Hong Kong and Department of Physics, Huazhong University of Science and Technology, Wuhan 430074, China

Hanchen Huang[a)]
Department of Mechanical, Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180

C. H. Woo
Department of Electronic and Information Engineering, Hong Kong Polytechnic University, Hong Kong

X. X. Zhang
Department of Physics and Institute of Nano Science and Technology, Hong Kong University of Science and Technology, Hong Kong

L. G. Zhou
Department of Mechanical, Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180

(Received 2 February 2004; accepted 7 May 2004; published online 17 June 2004)

This letter reports a mechanism of chemistry-mediated two-dimensional to three-dimensional (2D–3D) transition during In thin film deposition, and the corresponding evolution of nanoscale islands. Using magnetron sputtering technique, we deposit In on Au substrate. Despite the fact that In wets on Au, In islands prevail over the uniform film soon after the deposition starts. The 2D–3D transition is found to be a result of the formation of Au_3In on the Au substrate. The alloy formation leads to nonwetting of In, thereby the high mobility of In atoms and In clusters, and eventually well-separated In islands. The structures of In and Au are characterized by scanning electron microscopy, transmission electron microscopy, and electron diffraction. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1767595]

Three-dimensional (3D) islands may develop from the start of deposition or from a uniform two-dimensional (2D) thin film during deposition, because of strain energy.[1] In heteroepitaxy, strain may develop in the film due to film–substrate mismatch. Initially, the film grows layer-by-layer or in 2D mode. As the strain energy, which increases with film thickness, builds up to a critical value, the film growth goes through a 2D–3D transition and islands form to release the strain energy.[2] Quantum dots, also called artificial atoms, self-organize through this 2D–3D transition and pattern themselves to minimize the strain energy.[3] Such transition is of great interest both scientifically and technologically.[4] In addition to the strain energy, nonwetting also leads to islands formation, if film and substrate atoms dislike each other (or interact weakly). As a film is deposited on a nonwetting substrate, the film atoms try to minimize the number of bonds with the substrate and maximize that with other film atoms. Consequently, islands develop and 3D growth mode prevails at the beginning.[5] Even if a substrate is initially wetable, preprocessing may lead to the formation of a chemical compound which is nonwetting to the film.[6] A familiar example of the nonwetting phenomenon is oil droplet on water surface; the oil does not wet water and remains in droplet or 3D form. Summarizing the two mechanisms of 3D islands formation, we note that strain may lead to either 3D islands formation from the start of deposition or to 3D islands formation through a 2D–3D transition. In contrast, chemistry leads to 3D islands formation from the start only, but has not been known to lead to 2D–3D transitions.

This letter reports an experimental observation of chemistry-mediated transition of 2D–3D growth modes. The materials system is In film on Au substrate, which is predeposited on Si(111) or glass or carbon film. The experimental conditions are briefly summarized as follows. The magnetron sputtering deposition chamber is maintained at a base pressure of 5.0×10^{-8} Torr and a working pressure of 2.5×10^{-3} Torr through mechanical and turbo pumping. The sputtering power for indium and gold films are 25 and 10 W, respectively. The chamber is filled with 99.999% Ar, flowing into the chamber at a rate of 10 sccm. The targets are a block of 99.997% indium and a block of 99.999% gold, and are sputter cleaned in Ar gas for 5 min before deposition. The substrate, which is about 9 cm away from the target, is an *n*-type Si(111) wafer or glass or carbon film. In all cases, the wafer is cleaned ultrasonically in alcohol and then acetone. The deposition rates for In and Au are about 2.5 and 1.0 nm/s, respectively; the deposition rates are estimates based on film thickness measurement. The films are characterized using scanning electron microscopy (SEM, JEOL-6300F), transmission electron microscopy (TEM, JEOL-2010F), and the accompanying electron diffraction technique.

Shown in Fig. 1(a) is an SEM image of In islands, formed after 60 s of In deposition on an Au substrate of approximately 30 nm, which is predeposited for 30 s on the

---

[a)] Author to whom correspondence should be addressed; electronic mail: hanchen@rpi.edu

0003-6951/2004/84(26)/5401/3/$20.00

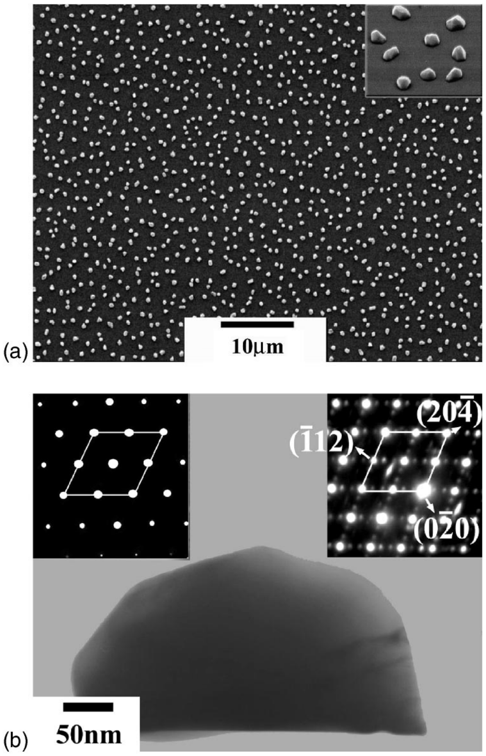

FIG. 1. (a) SEM image of In islands deposited on Au substrate at room temperature (at 60 s), with the expanded view of islands included as an inset. (b) Cross-section TEM image of an island, with the SAED patterns as insets; the left inset is theoretical and right experimental.

Si(111) substrate. These nanoscale islands are about 500 nm in diameter and 1000 nm away from each other. Further, the islands are covered with faceted surfaces, as shown in the inset of Fig. 1(a). A cross-section TEM image of one In island is shown in Fig. 1(b). The accompanying selected area electron diffraction (SAED) pattern is shown as the right inset. The set of bright spots correspond to the [201] axis, and another set of weak spots correspond to [110] axis. For easier comparison, the theoretical diffraction spots along the [201] axis are shown as the left inset. The agreement of these two electron diffraction patterns shows that the In island is a single crystal of [201] along the electron beam, with minute amount of grains of [110] and other orientations. The non-[201] grains are probably the clusters that merged at the early stage, as shown in Fig. 2(c). Similar results of In islands evolution are obtained when the Au substrate is predeposited on either glass or carbon film, indicating that the Au plays the decisive role. In the following, the analysis will focus on In-Au without regard to the supporting wafer (Si, glass, or carbon film).

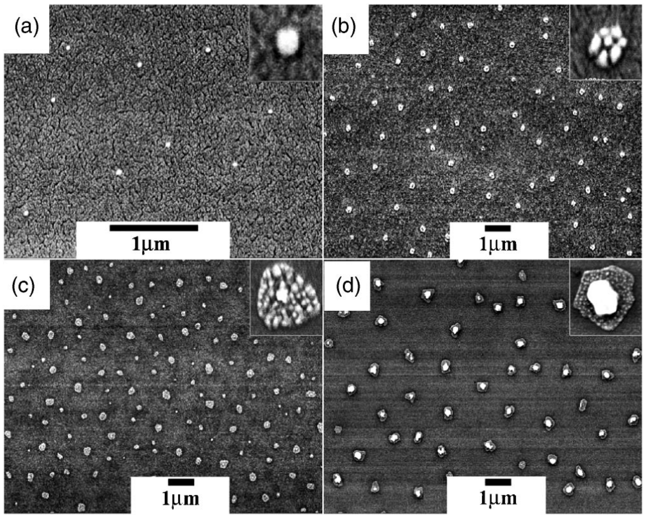

FIG. 2. SEM images of In islands on Au substrate, at 10 (a), 15 (b), 20 (c), and 25(d) s. The insets are expanded views of islands.

To understand the formation process of these islands, we examine the In deposition as a function of time. Shown in Fig. 2 are SEM images of the In film at about 10, 15, 20, and 25 s, respectively. The In film at 5 s is either uniform or in the form of islands that are too small to be visible. The SEM image at 5 s looks the same as the Au substrate—to be discussed in more detail later. Clusters of about 50 nm in diameter form at 10 s; as a convention, clusters are smaller than islands in this letter. Subsequently, the clusters segregate to form islands of about 200 nm by 15 s. The coalescence of these clusters indicates that they are highly mobile. Indeed, the high mobility is a necessary condition for the transition from the configuration of Fig. 2(a) to that of Fig. 2(b). In Fig. 2(b) (inset), coalesced clusters are not fully merged yet. The islands grow in size as deposition continues to 20 s. Further, new In clusters start to form on top of the islands, as shown in the inset of Fig. 2(c). The new clusters grow as deposition continues to 25 s, and they look like crystal nuclei [the inset of Fig. 2(d)]. These nuclei eventually grow into the faceted islands as seen earlier in Fig. 1(a). The faceted islands may serve as nuclei of future nanorods growth, but they are not the focus of this letter. Instead, the focus here is the mechanism of the 2D−3D transition.

The first possible mechanism is the conventional 2D−3D or Stranski–Krastanov growth. According to this scenario, the In film at 5 s is uniform. At 10 s the strain energy stored in the 25 nm In film and the 30 nm Au film must have reached a critical value, so the In film goes through a 2D−3D transition. Like in our earlier reports of Cu films,[7] intrinsic strain may build up to facilitate the transition. Not knowing the precise magnitude of strain energy, we tested its effects, by depositing either thicker Au film on the Au substrate or much thicker In film on a Si(111) substrate. If intrinsic strain energy is the driving force of the 2D−3D transition, it should also lead to similar transition in these two cases, in which films are thicker and thereby total strain energy is larger. As shown in Figs. 3(a) and 3(b), the 60 nm Au film has similar surface morphology as the 30 nm Au

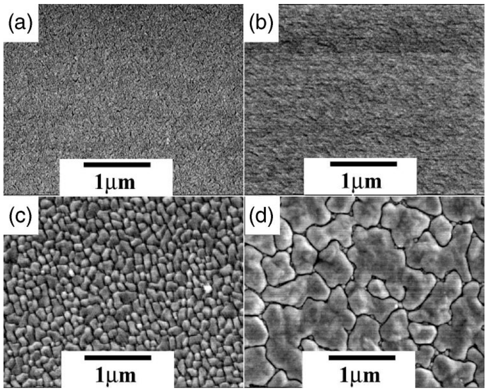

FIG. 3. SEM images of (a) 30 nm and (b) 60 nm Au films; and (c) 75 nm and (d) 150 nm In films on Si(111) substrate.

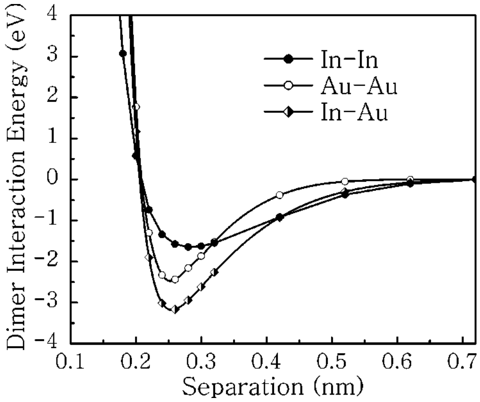

FIG. 4. Dimer interaction energy vs separation of the two participating atoms.

film (substrate), both being uniform. In passing, our x-ray diffraction data show that the Au film is primarily of ⟨111⟩ texture, as often observed. Compared to In, Au is much stiffer and has higher strain energy density for a given intrinsic strain. The absence of 2D–3D transition is an indication that strain energy is not the driving force of the transition in Fig. 2. In parallel to the thicker Au film, a thicker In film is also deposited on Si(111) substrate. The In film is uniform up to 75 or 150 nm in thickness, as shown in Figs. 3(c) and 3(d). Again, the absence of 2D–3D transition indicates that strain energy is not responsible for the transition in Fig. 2.

The alternative driving force of the 2D–3D transition is the nonwetting substrate. But it is known that In and Au form alloys and should wet each other. Our *ab initio* calculations also show that In–Au interaction is stronger than In–In or Au–Au interaction. The binding energy ratio of In–Au, Au–Au, and In–In dimers is 1.00:0.77:0.50, and energy-separation curves are shown in Fig. 4. The calculations are based on the same method as in Ref. 8, with a large supercell containing two atoms of variable separation. The binding energy difference is within 0.8% when the supercell goes from 30×30×60 a.u. to 40×40×80 a.u. in dimension; the supercell is longer along the dimer. The formation of alloys and the *ab initio* calculations confirm that In does wet on Au substrate. Then, there seems to be no conventional mechanism to explain the observed 2D–3D transition.

To positively identify the mechanism of In 2D–3D transition, we examine the film–substrate interface structures. Knowing the island structure (Fig. 1), we now focus on the film structure that leads to the island formation. The cross-section TEM image of the film after deposition of 5 s [Fig. 5(a)] shows two distinctive layers on top of the Si substrate. It is natural to attribute the middle layer to Au, since Au is deposited. Indeed, the lattice spacing of 0.235 nm corresponds to that of Au(111) plane, confirming the middle layer being Au. The top layer can be either In or one of the many In–Au alloys. The in-plane electron diffraction pattern of the area in Fig. 5(a) shows a ring in addition to those of Au; see Fig. 5(b). This ring matches that of $Au_3In(022)$ plane. The lattice spacing of 0.294 nm in Fig. 5(a) corresponds to $Au_3In(110)$ plane, and 0.340 nm to $Au_3In(011)$ plane. Combining the diffraction pattern and the lattice spacing, it is reasonable to attribute the top layer of Fig. 5(a) to Au_3In.

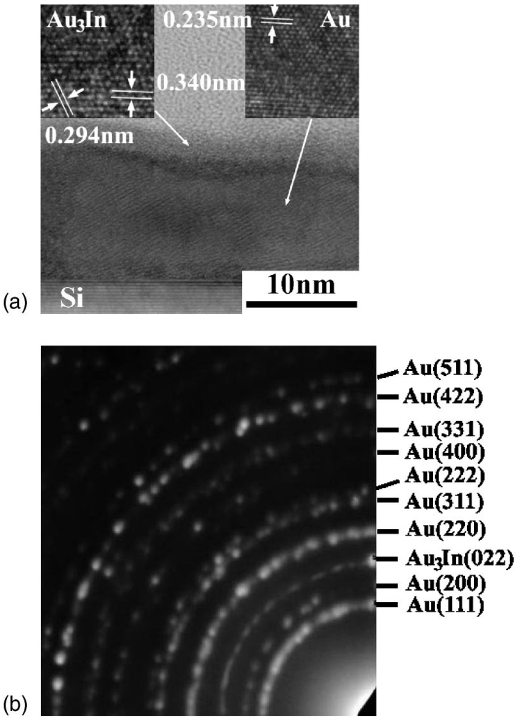

FIG. 5. (a) Cross-section TEM image of the In film at 5 s, with expanded views of Au and Au_3In as insets; and (b) the corresponding in-plane diffraction rings.

With the structure characterization, a mechanism of In 2D–3D transition emerges. The driving force is neither the strain energy nor the conventional nonwetting. Rather, the transition is chemistry-mediated. The initial 2D growth is associated with the Au_3In formation. Once this process is complete, the original wetting substrate (Au) turns into a nonwetting substrate (Au_3In) for In deposition. The chemical formation of Au_3In triggers the transition of In growth from 2D to 3D.

Before closing, a comment on the technological implication seems warranted. In addition to the scientific value, the mechanism of chemistry-mediated 2D–3D transition may be beneficial to the growth of nanorods. The single crystal In islands may serve as nuclei of nanorods growth. The realization of this technological implication remains to be explored.

The work at Hong Kong was supported by grants from the Research Grants Council of the Hong Kong Special Administrative Region (PolyU 5309/03E and 5312/03E, and HKUST 6165/01P). The work at Rensselaer Polytechnic Institute was partially supported through the Focus Center—New York, Rensselaer: Interconnections for Gigascale Integration.

[1] V. A. Shchukin and D. Bimberg, Rev. Mod. Phys. **71**, 1125 (1999).
[2] K. Brunner, Rep. Prog. Phys. **65**, 27 (2002).
[3] J. Tersoff, C. Teichert, and M. G. Lagally, Phys. Rev. Lett. **76**, 1675 (1996).
[4] D. Bimberg, M. Grundmann, and N. N. Ledenstov, *Quantum Dot Heterostructures* (Wiley, Chichester, 1999).
[5] J. C. Glueckstein, M. M. R. Evans, and J. Nogami, Phys. Rev. B **54**, R11066 (1996).
[6] A. C. Ferro and B. Derby, Acta Metall. Mater. **43**, 3061 (1995).
[7] H. L. Wei, H. Huang, C. H. Woo, R. K. Zheng, G. H. Wen, and X. X. Zhang, Appl. Phys. Lett. **80**, 2290 (2002); H. Huang, H. L. Wei, C. H. Woo, and X. X. Zhang, *ibid.* **82**, 4265 (2003).
[8] L. G. Zhou and H. Huang, Appl. Phys. Lett. **84**, 1490 (2004).