

Effect of surface reconstruction on the growth of self-assembled Ag nanostructures on Si(111) surfaces

Dipak K Goswami
Indian Institute of Technology Guwahati
Guwahati – 781039, India
e-mail: dkg@iitg.ernet.in

ABSTRACT

Thin Ag films of different thicknesses are grown on Si(111)-(7×7) surfaces at room temperature and then annealed at 700°C for 5 minutes. Ag films morphology evolution upon annealing has been investigated by scanning tunneling microscopy and interface structures are characterized by reflection high energy electron diffraction studies. Here we report the effect of interface structures on the growth of Ag films. Ag islands formed on Si(111)-(7×7) surfaces at room temperature with strongly preferred heights of even atomic layers keeping (7×7) reconstructed structure at the buried interface unaltered. However, upon annealing interface structures changes to (1×1) and Ag layer with single atomic layer heights following the Si steps are observed.

Keywords: Surface Reconstruction, Ag on Si(111), MBE, STM

1 INTRODUCTION

Study of metal-semiconductor interfaces has been of great interest for decades in view of their technological applications. The formation of thermally stable Schottky barrier is an important characteristic of many metal-semiconductor junctions. A large effort has been made to achieve the control of their electronic properties which are very important for microelectronic devices. In particular, the Ag/Si(111) system is one of the most extensively studied because it is a non-reactive metal-semiconductor system [1-3]. On the other hand, the study of low dimensional structures has attracted considerable interest because spatial confinement of electrons in thin films results in discrete quantum well states (QWS's). In the semiconductor layer systems, these effects are well known and have already been used in electronic devices. However, the observations of quantization effects in metal layers have been restricted to only a few systems. In this respect Ag films have attracted a great interest due to nearly free electron characteristics of s-p bands over a large region of Brillouin Zone (BZ). Nevertheless, the growth morphology of Ag on Si surfaces has been found to depend on the growth conditions. Therefore, this system becomes interesting to be explored further by researchers to

understand the fundamental aspects of the growth. A quasi-layer-by-layer growth were observed using reflection high energy electron diffraction (RHEED) measurement for Ag deposition on Si(111)-(7×7) surfaces at low substrate temperature (LT) for many monolayers (MLs) [4,5]. Room temperature (RT) growth of Ag was generally accepted as Stranski-Krastanov (SK) or layer-plus-island growth mode [6]. However, for RT deposition quasi-layer-by-layer growth has also been observed but only for high deposition rates (~30 ML/min) [4]. An LT growth of Ag on Si followed by RT annealing, leads to a new growth mode in which 3D plateau like Ag islands with strongly preferred height are observed on a wetting layer [7]. This growth mode is different from the conventional SK growth mode. The role of electronic driving force has been suggested to be responsible for this growth. Zhang and coworkers proposed the electronic growth mechanism, in which a uniform layer can be grown only over a thickness window; for film thicknesses below or above this window the metal film would be nonuniform [8,9].

Recently, we have reported the growth of Ag films on Si(111)-(7×7) surfaces for RT growth over a wide range of film thicknesses that showed plateau like percolated Ag islands with an N-layer where N is even (two, four, six etc) height preference [10,11]. N-layer height preference with even value of N is an effect of quantum confinement of electrons in the Ag islands. Some theoretical attempts have been made to understand the N-dependent stability of metal films in term of the energies of the quantum well states. These states are usually analyzed using a picture of standing wave formation within a potential well, in which energy dependent phase shift upon reflection at the interfaces is included as for s-p metals the QW energy levels are often described by the phase accumulation model [12,13]. Considering this growth feature, Ag growth on Si(111)-(7×7) at RT cannot be simply classified within the three commonly known growth modes such as layer-by-layer (Frank-van der Merwe, FM), layer-plus-island (Stransky Krastanov, SK) and island (Volmer-Weber, VW) growth modes. Dynamics of this growth mechanism has also been studied and different scaling exponents associated with such growth mechanism have been calculated [12]. However, understanding of this growth mechanism is not completed fully and we have explored the effect of buried interface structures on the growth mechanism. In this report, we have shown that Si(111)-(7×7) reconstructed

surfaces plays important role for preferential height growth of Ag. As long as (7×7) surface structure is preserved at the buried interface, Ag grows with even layer height preference. It has been shown that RT growth of Ag on Si(111)- (7×7) surfaces protect the (7×7) reconstruction at the interface. However, upon annealing reconstruction at the interface changes and therefore, preferential height growth vanishes. We have grown Ag films with different thickness on Si(111)- (7×7) surfaces at RT. Scanning tunneling microscopy (STM) and RHEED measurements were carried out for morphology and structural characterization. RT growth samples were annealed at higher temperatures. Interfaces structures are probed using RHEED measurements.

2 EXPERIMENTAL

Growth of Ag films on Si(111)- (7×7) surfaces and STM measurements to study the morphology of the Ag films were performed in a custom made molecular beam epitaxy (MBE) chamber coupled with an ultrahigh vacuum (UHV) variable temperature scanning tunneling microscope (VTSTM, Omicron Nanotechnology) at Institute of Physics in Bhubaneswar [15]. Base pressure in the growth chamber was 1×10^{-10} mbar. Si(111) substrates were cut from n-type silicon wafers with resistivity in the range 10-20 Ωcm . These Si samples contain a amorphous oxide layer of 15 - 20 \AA thickness. After introducing into the MBE chamber, substrates were degassed at 600°C for about 12 hours to remove the adsorbed gas and water molecules. The samples were then flashed briefly at 1150°C to remove native oxide layer and cooled it down slowly to RT. This produces atomically cleaned reconstructed surfaces. Si(111)- (7×7) reconstructed surfaces were observed by RHEED and STM. Atomically cleaned surfaces were used to study the Ag growth. Ag atoms were evaporated from Kudsens cells (PBN Crucible) and deposited onto the Si(111)- (7×7) surfaces, kept at RT, at the rate of 2ML/min. During the deposition the chamber pressure increased to 8.5×10^{-10} mbar. After the growth, RHEED measurements were carried out to study the atomic arrangements of the deposited atoms. Sample was then transferred into the VTSTM chamber for microscopy measurements. We have deposited 2 and 4ML Ag on Si(111)- (7×7) surfaces for this measurement. This thicknesses were chosen within the thickness window where we have observed percolated flat top Ag islands and at the same time, even atomic layer preferential height growth were strictly maintained [10]. For the annealed samples, annealing at 700°C for 5 minutes was performed following deposition in the MBE chamber. Before the samples were transferred to STM chamber, RHEED measurements were carried out.

3 RESULTS AND DISCUSSIONS

Depending on the preparation conditions Si(111) can form $(2n + 1) \times (2n + 1)$ surface reconstructions, where

$n=1,2,3\dots$. Out of all these reconstructions the (7×7) reconstructed surface is the most stable surface. The driving force for the formation of the (7×7) reconstruction is the reduction of the number of dangling bonds by the formation of dimers, adatoms and stacking fault. This accepted structural model of the Si(111)- (7×7) reconstructed surface is known as dimer-adatom-stacking-fault (DAS) model and was proposed by Takayanagi et al. in 1985 [24]. Fig.1(a) shows STM image of Si(111)- (7×7) and was taken at

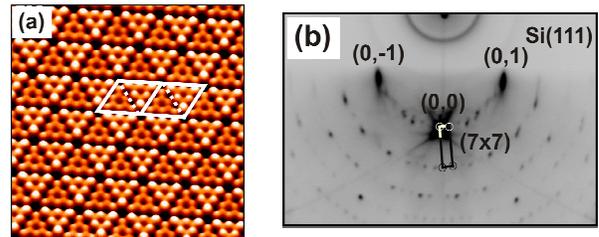


Fig 1 (a) STM image of a Si(111)- (7×7) surface with sample bias of -2.23V and tunneling current of 0.20 nA . Two (7×7) unit cells are marked. This image does not show any atomic defects. (b) RHEED pattern from atomically clean Si(111)- (7×7) . Marked bright spots are from (1×1) bulk Si(111) lattice. Seven less bright spots appeared are from (7×7) surface unit cells. One (7×7) unit cell in reciprocal space is marked.

a negative sample bias voltage which corresponds to electrons tunneling from the filled states of the sample into the tip. Here the adatoms in the half unit cell with stacking fault are imaged brighter than the adatoms in the other half without stacking fault. Two such unit cells which are 7 times larger than Si(111)- (1×1) unit cell are also marked. The RHEED pattern from this surface also shows the (7×7) reconstruction as seen in Fig.1(b). Six fractional-order spots appeared in between the integral order spots from the bulk. This signifies the (7×7) reconstructed surfaces. Bulk Si(111) spots are also indicated in figure by arrow. (7×7) unit cell in reciprocal space is also marked. Other reconstruction on Si(111) surfaces are also observed as for example, formation of (2×1) reconstruction is reported on the cleaved Si(111) surface [16]. Ag is found to grow epitaxially on silicon in spite of the large lattice mismatch (25%) [17-19]. Apparently, this is made possible by coincident site lattice matching as the lattice mismatch between $3a_{\text{Si}}$ and $4a_{\text{Ag}}$ is only 0.43% ($a_{\text{Si}} = 5.43\text{ \AA}$; $a_{\text{Ag}} = 4.09\text{ \AA}$ [17, 20, 21]. Coincident site lattice matching alone does not give rise to epitaxial growth. There should be favorable bonding configuration of the substrate and over layer atoms at the interface. For example, Al grows epitaxially on Si(111) but not on Si(100) [22]. Even though there is coincident site lattice matching in both the cases, there is a favorable bonding configuration only for Al(111)/Si(111). Ag is found to grow epitaxially on both Si(111) and Si(100) surfaces with Ag(111)||Si(111), Ag(100)||Si(100) and Ag(111)||Si(100) [23].

Si(111)-(7×7) surface is very sensitive to a little amount of metal atom adsorbates. The amount of adsorbates is expressed mainly in units of monolayer (ML) which corresponds to one adsorbate atom for each (1×1) unit cell of the ideal non-reconstructed substrate surface, which has one atom per unit cell. A monolayer is a relative value associated with the given substrate. In general, for a given surface the surface atomic density (number of atoms/cm²) is a monolayer. For Ag on Si(111), two definitions of an ML have been used in the literature. In one definition an ML is 0.78×10^{15} atoms/cm² [the atomic density on an ideal Si(111) surface] and in the other 1.5×10^{15} atoms/cm² [the atomic density on an ideal Ag(111) surface]. We have taken the latter one as the definition of ML. The presence of the foreign atoms at elevated substrate temperatures can cause the surface to change its two-dimensional periodicity, vary the spacing between atoms and change electronic properties of the surface. Si(111)-($\sqrt{3} \times \sqrt{3}$) R30°-Ag is one such common surface obtained by deposition of Ag on a Si(111)-(7×7) upon annealing at temperatures above 200°C. We have annealed the 0.5 ML Ag film at 260°C. This is the early stage of the $\sqrt{3}$ surface phase formation. The most interesting feature is that the phase grows in two associated domains called a hole-island pair as seen earlier [24]. The hole (seen as the dark area) and the island are the $\sqrt{3}$ structures with one atomic step height difference [3.14 Å or one Si(111) bilayer separation]. However, Ag growth on Si(111)-(7×7) at RT does not change the substrate reconstruction. In our RHEED experiment for 1 ML Ag growth, we have observed (7×7) interface structures. Although the intensities of both the integral and the fractional order spots are greatly reduced compared to the bare Si(111)-(7×7) surface (as shown in Fig.1(b)), the (7×7) reconstruction still persists. In addition the integral order spots from a Ag(111) surface appear. This indicates that Ag grows with (111) planes parallel to the surface on top of Si(111)-(7×7) surface. Earlier a X-ray diffraction results showed that even after deposition of a 260 Å thick Ag film on Si(111)-(7×7) reconstruction, in the buried interface the (7×7) structure is preserved. There might be some modifications of the Si adatom symmetry as they are the most loosely bound atoms in the (7×7) unit cells [25-27]. RT growth of Ag on Si(111)-(7×7) surfaces form flat top islands with even atomic layer height preference [10]. These flat top islands start percolating with further Ag growth. Interestingly, Ag atoms grow on (7×7) surfaces without changing the interface structures. Exact atomic relationship between Si and Ag atoms at the interface is, however, not known. Upon annealing these percolated structures at 700°C for 5 minutes produce single atomic layer height following the clean silicon steps and the interface becomes (1×1). This is contrasted by the Si(111)-($\sqrt{3} \times \sqrt{3}$)R30° structure formed by annealing a thin Ag film on Si(111). Annealed thick Ag film at RT the ($\sqrt{3} \times \sqrt{3}$)R30° reconstruction is suppressed [25]. The ($\sqrt{3} \times \sqrt{3}$)R30° reconstruction obtained by annealing is a surface structure, having nothing to do with the buried interface.

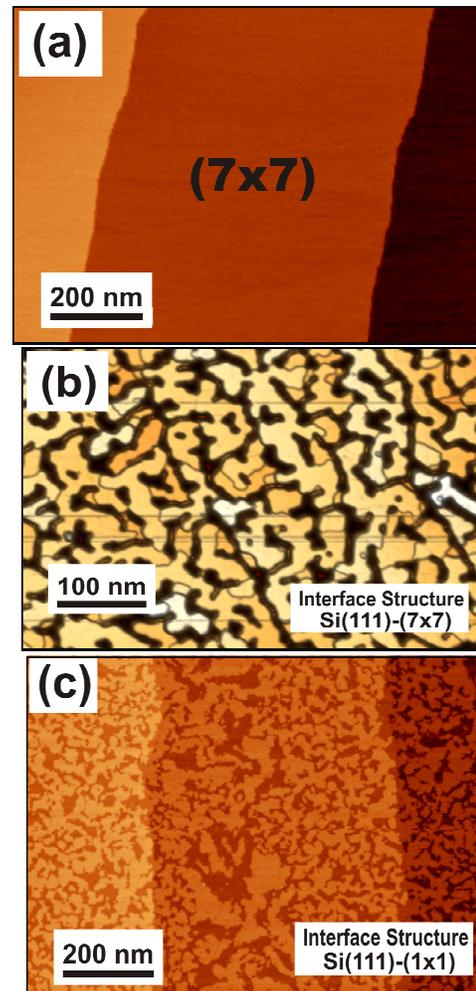


Fig 2 (a) STM image of atomically clean Si(111)-(7×7) surface steps. Three such steps are shown. (b) STM image of 2 ML Ag RT grown on Si(111)-(7×7) shows flat top percolated Ag islands. (c) Upon annealing at 700°C for 5 min shows the Ag steps with fractal like structure.

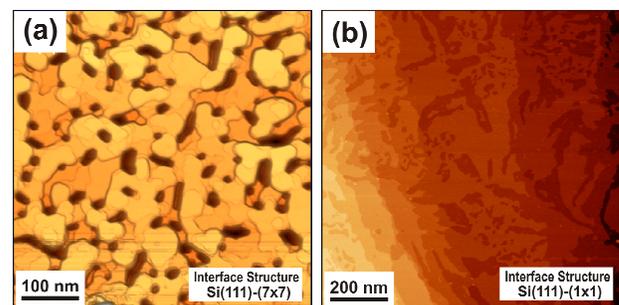


Fig 3 (a) STM image of 4 ML Ag RT grown on Si(111)-(7×7) surfaces. (b) Ag atomic steps are seen after annealing at 700°C.

Fig.2(a) shows STM image of clean Si(111)-(7×7) surface with three steps. 2 ML Ag deposited on to this surface at RT. Flat top percolated Ag islands are formed as

shown in Fig.2(b). Even atomic layer height preference was observed for RT growth as per our earlier report [10]. Upon annealing at 700°C for 5 minutes of the flat top Ag islands produces Ag single atomic steps with fractal like structures which are apparently following Si(111) steps underlying film as shown in Fig.2(c) where Ag monatomic steps forming fractal like structure are clearly seen. In this case, interface structures changes to (1×1) from (7×7) due to annealing which was confirmed by RHEED measurements. Fig.3(a) shows STM image of 4 ML Ag growth deposited on to Si(111)-(7×7) surface at RT. Ag atomic steps are also observed after annealing as shown in Fig.3(b) as like 2 ML sample. However, Ag atomic layer become more uniform because of higher Ag coverage and therefore large Ag terraces are observed. Interesting features of this observation is that the buried interface structure of Si(111) surfaces are changed upon annealing. This change at the interface plays important role to the growth of the Ag overlayer as we observed preferential growth to single atomic layer fractal like growth. Moreover, preferential even atomic layer growth which is apparently a metastable state of Ag growth only exist on the (7×7) surfaces.

In conclusion, we have studied the role of buried interface structure of Si(111) surfaces on the growth of Ag overlayer. We have deposited two coverage of Ag on Si(111)-(7×7) at RT and annealed at 700°C for 5 minutes. In both the case, we observed that even atomic layer preferential growth that was observed in our earlier studies changes to single atomic layer growth with fractal like morphology as the interface structures changes from (7×7) to (1×1) upon annealing.

4 ACKNOWLEDGEMENTS

Author would like to acknowledge Institute of Physics, Bhubaneswar where these experiments were carried out. It is pleasure to thank Prof. B. N. Dev and Prof. P. V. Satyam for their valuable discussions and help during the experiments.

5 References

[1] S. Hasegawa, X. Tong, S. Takeda, N. Sato, T. Nagao, *Prog. Surf. Sci.*, 60, 89 (1999);
 [2] W. G. Schmidt, F. Bechsted, G. P. Srivastava, *Surf. Sci. Rep.*, 25, 141 (1996).
 [3] E. J. Leonen, M. Iwami, R. M. Tromp and J. F. van der Veen, *Surf. Sci.*, 137 (1984) 1.
 [4] Z.H. Zhang, S. Hasegawa, S. Ino, *Phys. Rev. B* 55 (1997) 9983.
 [5] K.R. Roos, M.C. Tringides, *Surf. Sci.* 302 (1994) 37.
 [6] C. Argile, G.E. Rhead, *Surf. Sci. Rep.* 10 (1989) 277
 [7] L. Gavioli, K.R. Kimberlin, M.C. Tringides, J.F. Wendelken, Z. Zhang, *Phys. Rev. Lett.* 82 (1999) 129.
 [8] Z. Zhang, Q. Niu, C.-K. Shih, *Phys. Rev. Lett.* 80 (1998) 5381.
 [9] Z.G. Suo, Z.Y. Zhang, *Phys. Rev. B* 58 (1998) 5116.
 [10] D.K.Goswami, K. Bhattacharjee, B. Satpati, S. Roy, P.V.Satyam, B.N.Dev, *Surf. Sci.* 601 (2007) 603

[11] D.K.Goswami, K. Bhattacharjee, B. Satpati, S. Roy, G.Kuri, P.V.Satyam and B.N.Dev, *Appl. Surf. Sci.* 253 (2007) 9142.
 [12] T.-C. Chiang, *Surf. Sci. Rep.* 39 (2000) 181.
 [13] C.M.Wei, M.Y. Chou, *Phys. Rev. B* 68 (2003) 125406; *Phys. Rev. B* 66 (2002) 233408.
 [14] D. K. Goswami and A. Pal (2010, communicated)
 [15] 10. D. K. Goswami, B. Satpati, P. V. Satyam and B. N.Dev, *Curr. Sci.* 84 (2003) 903.
 [16] K. C. Pandey, *Phys. Rev. Lett.*, 47, 1913 (1981).
 [17] G. A. Smith, K.-H. Park, G.-C. Wang, T.-M. Lu and W. M. Gibson, *Surf. Sci.*, 233, 115 (1990)
 [18] D. C. McKenna, G.-C.Wang and K. Rajan, *J. Electronic Matter*, 20, 753 (1991).
 [19] K. Takahiro, S. Nagata and S. Yamaguchi, *Appl. Phys. Lett.*, 69, 2828 (1996).
 [20] T. C. Nason, L. You, G.-R. Yang and T.-M. Lu, *J. Appl. Phys.*, 72, 466 (1992) and references therein.
 [21] T. J. Konno and R. Sinclair, *Phil. Mag.*, 71, 163 (1995).
 [22] F. K. LeGoues, W. Krakow and P. S. Ho, *Phil. Mag.*, A53, 833 (1986).
 [23] F. K. LeGoues, M. Liehr, M. Renier and W. Krakow, *Phil. Mag.*, A57, 179 (1988).
 [24] A. Shibata, Y. Kimura, K. Takayanagi, *Surf. Sci.*, 275, L697 (1992).
 [25] H. H. Hong, R. D. Abrano, D.-S. Lin, H. Chen, T.-C. Chinag, P. Zschack and E. D. Specht, *Phys. Rev. Lett.*, 68, 507 (1992).
 [26] R. D. Abrano, H. Hong, J. M. Rosler, K. Chang, D.-S. Lin, P. Schach and H. Chen, *Phys.Rev.*, B52, 1839 (1995).
 [27] K. Akimoto, M. Lijadi, S. Lto and A. Ichimiya, *Surf. Rev. Lett.*, 5, 719 (1998).