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Two-dimensional growth of Al films on Si(1 1 1)-7 × 7 at low-temperature

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Abstract

Morphology and structure of the Al(1 1 1) films, grown on Si(1 1 1)-7 × 7 surface at both low (145 K) and room temperature, are investigated by in situ reflection high-energy electron diffraction (RHEED) and scanning tunneling microscopy (STM). In the low-temperature case, a well-defined critical thickness of 4 ML, at which atomically flat Al films with remarkable stability form, is identified. The formation of the flat film at the critical thickness completes the Al/Si(1 1 1) interface, and results in a subsequent homoepitaxial-like layer-by-layer growth for the entire Al coverages studied. The results are consistent with the formation of the quantum well states (QWS) recently observed in this system, and typify another intriguing example of quantized electronic states in tailoring thin film growth.

Keywords: Growth; Aluminum; Silicon; Molecular beam epitaxy; Scanning tunneling microscopy; Reflection high-energy electron diffraction (RHEED); Quantum wells

1. Introduction

Layer-by-layer growth of epitaxial thin film is highly desirable in many cases in terms of both basic research and technological applications, and great progress has been made in semiconductor-on-semiconductor and metal-on-metal epitaxy [1,2]. For a metal deposited on another metal substrate, observation of reflection high-energy electron diffraction (RHEED) intensity oscillations has clearly shown that layer-by-layer growth is possible even at temperatures below 100 K [3]. However, due to stress effects and chemical mismatch, growing an ideal metal overlayer on a semiconductor has proved to be much more difficult.

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The most commonly observed growth mode for non-reactive metal/semiconductor interfaces is the formation of three-dimensional (3D) islands with varying sizes, either directly on a clean substrate (Volmer–Weber growth) or after completion of a wetting layer (Stranski–Krastanov growth). Nevertheless, efforts to achieve a sharp interface have continued because an ideal metal-semiconductor interface provides also a testing ground for many theoretical models, besides its application significance. Recently, a two-step method (low-temperature (LT) deposition followed by thermal annealing to room temperature (RT)) has attracted wide attention [4], since growth kinetics associated with this method allows formation of perfectly flat 2D films with apparent wetting property, even for the systems that are non-wetting [4–6]. In this case, undesirable kinetic processes are bypassed, and a non-equilibrium structure formed at LT drives the system to an intermediate metastable state with magic thickness, which is inaccessible if growth is thermally activated. A novel "electronic growth" mechanism was developed theoretically, in which the energy contribution of the quantized electrons confined in the metal overlayer can actually determine the film morphology, prevailing over the strain energy [7]. However, little is known whether such electronic stabilization is general for non-reactive metal/semiconductor system.

A recent study by Aballe et al. shows the growth of a crystalline (1 1 1)-oriented Al films on Si(1 1 1) with an abrupt and homogeneous interface at LT [8]. The quantum well states (QWS) could be observed for Al films up to 30 monolayers (ML) by angle resolved photoelectron spectroscopy (ARPES). The study raises several interesting questions from a point view of thin film growth. For example, how does the surface morphology evolve as a function of Al coverage, what kind of mechanism leads to such novel growth mode? As observation of QWS requires very sharp interface and surface morphology, atomic-scale information is important for understanding these issues, which is the subject of the present work.

In this study we report on an intriguing 2D growth of Al films on Si(1 1 1)-7 × 7 surface at 145 K. We have identified a characteristic critical thickness of 4 ML, at which the film is atomically flat and exhibits remarkable stability. Once it forms, subsequent growth is two-dimensional, which, we believe, is essential for the observation of QWS in this system [8]. Based on a comparison between in situ RHEED patterns and corresponding STM images, we argue that the novel growth is governed mainly by the energy quantization of the confined electrons in the metal thin film, which is different from Ag/GaAs [4], neither Al/Si(1 1 1) system deposited at RT [9,10]. The former was obtained using a two-step method where very small clusters firstly formed at LT and then rearranged into flat film at a coverage more than the critical thickness when annealing to RT. In the latter case, three-dimensional growth mode is dominated (the deposited Al atoms immediately form 3D islands) at RT.

2. Experimental

An OMICRON ultra-high vacuum STM system combined with molecular beam epitaxy was used in this study. The base pressure of the system is better than 1×10^{-10} Torr. The substrates were n-type Si(1 1 1) wafers with a resistivity of 8–20 mΩ cm. The clean 7 × 7 reconstructed surface was obtained by the well-established annealing and flashing procedures. During growth, the substrate was cooled to ~145 K by a copper block with two liquid nitrogen vessels. The temperature was measured with a NiCr–NiAl thermocouple close to the sample, with an error of approximately ±5 K for any given temperature. Aluminum was evaporated from a PBN crucible with a flux rate of 0.17 ML/min. In situ RHEED patterns were recorded in the $[11\bar{2}]$ azimuth of the Si(1 1 1)-7 × 7 surface with an electron beam energy of 12 keV at a glancing incidence angle. After the growth at LT, the samples were allowed to warm-up naturally to RT for 0.5–1 h, and then the STM topographic images were recorded at RT. We did not observe significant change in the STM images at different sample voltages, so all images presented correspond to the occupied states acquired at −1.8 V with a tunneling current of 30 pA.

3. Results and discussion

Fig. 1 shows the RHEED patterns during Al growth at 145 K for the Al coverages of 0, 1, 3 and 4 ML, respectively. Compared to the clean surface (Fig. 1(a)), the 7 × fractional diffraction streaks become very weak after 1 ML Al was deposited (Fig. 1(b)), and disappear completely at 2 ML (not shown). At 3 ML, a 1 × like long but broad streaks appears. These results indicate that an ordered Al layer starts to form on top of a featureless wetting layer with ~2 ML thickness. The long streaks become sharp as the Al coverage increases to 4 ML. The lattice constant of the Al films, as measured from the RHEED pattern, is ~2.86 Å, the same as that of the bulk Al(1 1 1), which is consistent with formation of a crystalline and relaxed Al films with an epitaxy relationship of Al(1 1 1)||Si(1 1 1) and Al[$1 1 \bar{2}$]||Si[$1 1 \bar{2}$]. During further deposition (up to 30 ML), the RHEED pattern essentially remains streaky and sharp. A layer-by-layer growth should be expected. Furthermore, there is very little change in the diffraction pattern when the samples were warmed from 145 K to RT, and thus the films formed at and after 4 ML are rather stable.

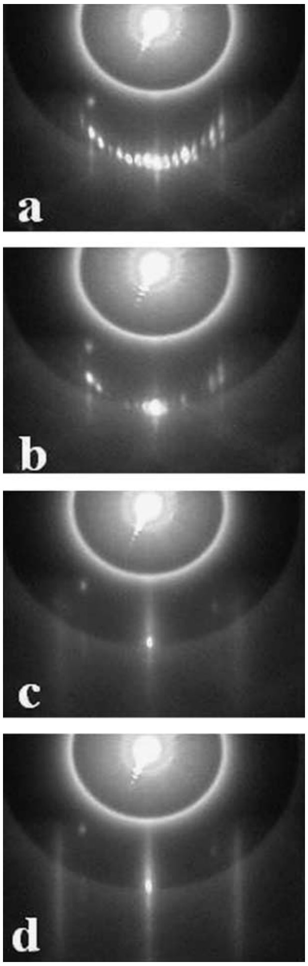

Fig. 1. In situ RHEED patterns for (a) 0, (b) 1, (c) 3, (d) 4 ML Al deposited on Si(1 1 1)-7 × 7 surface at 145 K, respectively.

Fig. 2 shows the typical STM topographic images of the Al films formed at the coverages from 1 ML to 8 ML. At 1 ML Al coverage (see Fig. 2(a)) the substrate is completely covered by Al nanoclusters with diameters from 3 nm to 6 nm and heights of up to 0.5 nm. This disordered structure (marked as A) forms a wetting layer for subsequent Al growth, which is still visible in the dark areas in Fig. 2(b)–(d). When the coverage increases to 2 ML (Fig. 2(b)), besides the 3D clusters mentioned above, small flat 2D islands with a single atomic-layer height appear on the wetting layer. We call these 2D islands as the first Al overlayer (marked as B) on top of the wetting layer (A). At 3 ML, the B-type 2D islands grow laterally and interconnect together (see Fig. 2(c)). Moreover, before completion of the first overlayer (B) on top of the wetting layer (A), a second overlayer (marked as C) also with a flat-top starts to grow locally on the first overlayer (B). This is probably a sign of typical multi-lever 3D growth where atomic mass transport between levels C to B is insignificant due to the Ehrilich–Schwoebel (ES) barrier and limited kinetics at LT. Thus, one would expect that, with further deposition, a multi-level morphology with many 3D islands would be developed, leading to a rough surface.

Surprisingly, this is not the case—what we observed is an atomically flat film when 4 ML Al was deposited (Fig. 2(d)). No third overlayer forms before the second overlayer (C) is completed. To illustrate the morphology evolution more clearly, we present the corresponding height histograms of the STM images at 3 ML and 4 ML in Fig. 2. The heights of “B” and “C” can be extracted

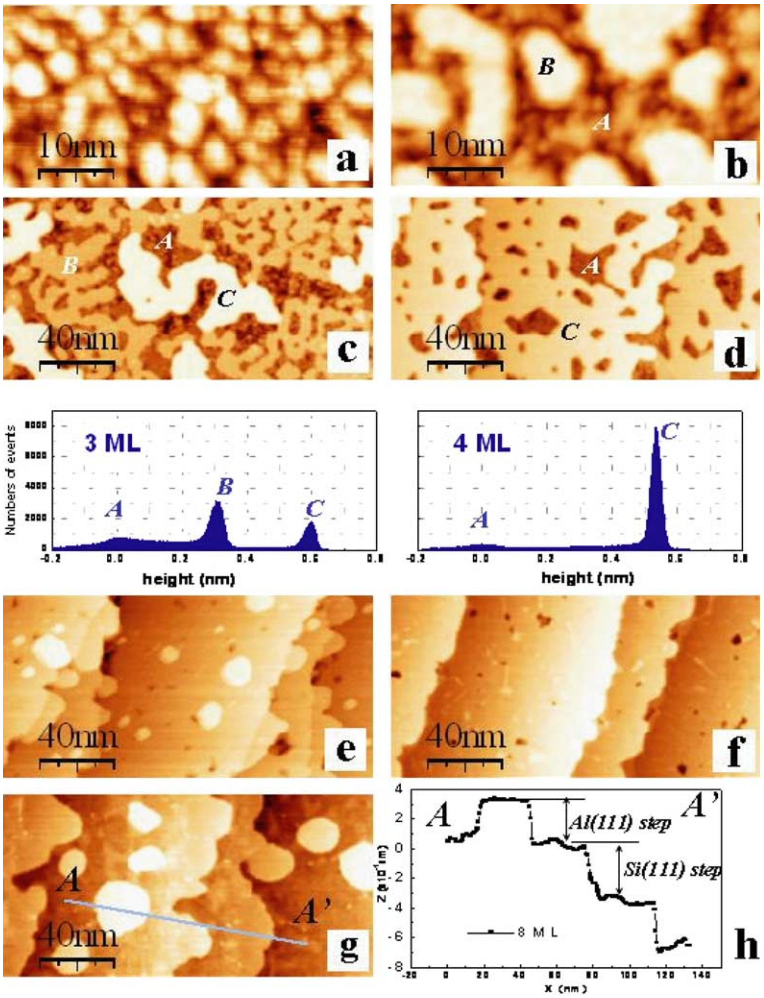

Fig. 2. The RT STM images for the Al films at different coverages (a) 1 ML; (b) 2 ML; (c) 3 ML; (d) 4 ML; (e) 5 ML; (f) 6 ML; (g) 8 ML. The image size for (a,b) is $25 \times 50\,\text{nm}^2$, for (c–g) is $100 \times 200\,\text{nm}^2$. (b, c) also include the corresponding island height distribution, respectively. Peak A, B and C represent the Al wetting layer, the first Al(1 1 1) overlayer and the second Al(1 1 1) overlayer, respectively, which are all marked in the corresponding STM images. The height profile along the AA′-line marked in (g) is shown in (h). Steps in the Si(1 1 1) substrate and the Al(1 1 1) monolayer island are labeled in the figure.

relative to that of "A" (i.e. the height of the wetting layer). At 3 ML coverage, apart from peak A, we can see a stronger peak B and additional peak C with 1 ML and 2 ML heights, respectively. At 4 ML, peak B disappears completely and only peak C exists, which, once again, verifies that the second overlayer (C) on top of the wetting layer is very special. The two steps running vertically in the STM image (Fig. 2(d)) correspond to the single atomic-layer height of Si(1 1 1), and thus the overall morphology is simply a duplication of the Si substrate. Appearance of some voids, where the wetting layer (A) is still observable, is due to incomplete full-monolayer deposition of the Al. Indeed, further deposition of the right amount of Al leads to the formation of an atomically flat and complete film at this critical thickness.

Once this stable Al layer forms, subsequent growth is found to proceed in a 2D and homoepitaxy-like mode. This is illustrated in Fig. 2(e)–(g) for the coverages of 5, 6 and 8 ML, respectively. Small islands appear on the large Al terraces defined by the Si substrate, which can be clearly seen by the line profile of AA′ in Fig. 2(h). From the meandering nature of the steps shown in Fig. 2(e)–(g), it seems that step advancement is the predominate atomic process, despite of nucleation of some 2D islands on terraces. The deposited atoms migrate sufficiently enough so as to cross the terraces and incorporate to the step-edges of low terraces. This leads to an outward propagation or ‘‘flow’’ of the steps on the low terraces. The surface morphology on a larger scale is very flat, and the root-mean square roughness (w_{rms}) of the surface (Fig. 2(f)) is only 0.5 Å. The results agree well with the RHEED observations, as discussed above. Note that the Al islands and films are only metastable: Upon annealing at 500 K and above, they both evolve into huge mounds and pyramids, which is similar to the morphology obtained in the SK growth mode at RT [9].

Fig. 3(a)–(c) show the close-view STM images of the Al films for 2, 3 and 4 ML coverages, respectively, which confirm that the films have a hexagonal close-packed structure and the same orientation as that of the substrate, in agreement with the RHEED observation. The separation between the neighboring bright dots is 2.7 nm, almost identical to the unit cell size of the clean Si(1 1 1)-7 × 7 reconstruction, as typified by the schematic in Fig. 3(b). This corresponds to approximately 9 times of the Al(1 1 1) plane lattice constant (0.286 nm) with a ‘‘domain mismatch’’ of ∼4.3%, similarly calculated in Ref. [9]. Fig. 3(a) illustrates that this superstructure already formed in the first B-type overlayer on the wetting layer. This structure becomes dominating when the coverage increases to 4 ML, which, again, agrees with the RHEED observation where an Al bulk 1 × 1 structure was observed (Fig. 1(d)). Compared to the 3 × 3 superstructure of the Al film formed at RT [9], the periodicity of this superstructure is almost the same as that of Si substrate, which reveals a stronger effect from the substrate at LT.

For comparison, we have deposited Al on Si(1 1 1)-7 × 7 at RT, as shown in Fig. 4. Similar to previous studies [9], compact and flat-top

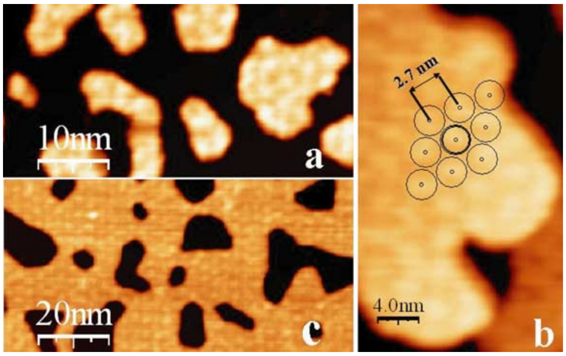

Fig. 3. The STM images of the Al films for (a) 2, (b) 3 and (c) 4 ML Al coverages, respectively. The image size is $20 \times 34\,\mathrm{nm}^2$ (a), $25 \times 50\,\mathrm{nm}^2$ (b), and $50 \times 100\,\mathrm{nm}^2$ (c), respectively. Hexagonal close-packed structure is shown, where the separation between the big bright dots is about 2.7 nm.

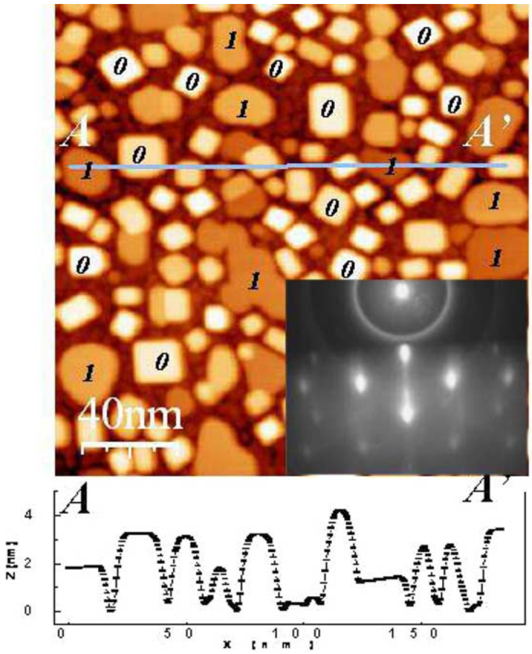

Fig. 4. The STM image ($200 \times 200\,\mathrm{nm}^2$) displaying the morphology of the Al films at 4 ML deposited at RT. The profile along AA′-line marked in the figure shows a very rough surface. Compact and flat-top islands are separated by narrow and thin grooves. The islands with rectangular- or round-shape are (0 0 1) and (1 1 1) oriented, as marked by ‘‘0’’ and ‘‘1’’, respectively. The inset is the corresponding RHEED pattern, which further clearly indicates the formation of both (1 1 1) and (0 0 1) oriented islands.

islands separated by narrow and deep grooves are observed, and the islands are both (1 1 1) and (0 0 1) oriented, as marked by "1" and "0", respectively. The inset is the corresponding RHEED pattern, which further clearly indicates the formation of both (1 1 1) and (0 0 1) oriented islands. Although there exists an argument on the nature of the interface (whether sharp or reacted) [8–10], we believe that for the (1 1 1) oriented islands, the interface structures prepared by two different methods should be very similar. The difference in morphology and thus residual strain implies that additional mechanism is responsible for the stability of the very flat film obtained at LT.

The 2D growth mode has been observed for many metal/metal and some metal/semiconductor systems, such as Ag and Pb on Si(1 1 1)-7 × 7, at LT [5,6,11]. Since thermally activated diffusion, the most important factor governing growth at elevated temperatures, is largely suppressed at LT, some non-thermal mechanisms, such as transient mobility, island-size-dependent diffusion barrier, and funneling [2], may be responsible for the present morphology. When Al is deposited on the clean Si surface at LT, the Al atoms may stay where they land due to the Al-Si interaction and limited diffusion, a homogeneous but featureless wetting layer is resulted. Thus, no streaks can be expected, but the 7 × 7 symmetry should be still observable (Fig. 1(b)). When more than 1 ML Al are deposited, even at LT clustering may happen after substrate is passivated by the first wetting layer due to the enhanced Al-Al interaction, high-density nucleation sites will form. With further deposition, some of the sites might convert to small Al islands. The results agree with the ARPES study of this system. The featureless nature of the film surface that is made up of homogeneous clusters/small islands should lead to disappearance of the Si(1 1 1) surface states, and no defined QWS can be expected [8]. If the process continues, the islands will become bigger and the surface becomes rougher. The fact that the system selects a very flat morphology at 4 ML (Fig. 2(d)) suggests the thermodynamic force due to the formation of QWS [8] plays an important role in the growth, since surface roughening will kill the QWS and should be energetically unfavorable. However, the kinetic factors for achieving this flat morphology favored by quantum size effects are still unknown, and more work is needed.

As a result of the formation of flat film at the critical thickness, further growth can be regarded as an Al/Al(1 1 1) homoepitaxy with very small in-plane and exchange diffusion barrier [12,13]. Given that most strains are released at the interface, the low barriers explain the step-flow like growth at the regime above 4 ML (Fig. 2(e)–(g)).

The critical thickness of 4 ML can be well understood from the electron confinement effect. According to the definition used in Ref. [7], the critical thickness is a thickness at which a stable flat film fully covers the substrate. Within the concept of "the electronic growth model", the critical thickness of a metal film is determined primarily by two competing processes. The first is the quantum confinement of electrons in the metal overlayer [8], which leads to an energy increase in the film. The second is the charge transfer from the metal to the substrate that causes an energy decrease. The competition between these two effects determines the total energy as a function of film thickness and thus defines a critical thickness. For Al on GaAs(1 1 0), the critical thickness is predicted to be 5 ML [7]. In the present case, the existence of the Fermi level pinning enhances the charge transfer [14]. Thus, a thinner thickness is expected, in agreement with our experiments.

Electron confinement effect also stabilizes the film upon warming-up to RT, as observed both by RHEED and STM. The warming-up process is seen not to cause a distinct change in the morphology, especially for the films with more than 4 ML Al, and thus all changes (lateral ordering) are limited within the same layer level (Fig. 2(a)–(d)). This is different from what happened in the Ag/GaAs(1 1 0) system, where the morphology changes dramatically when annealed to RT. Theoretical studies have pointed out that the confined electrons within a metal film could mediate a surprisingly long-range force to stabilize metal films of many atomic layers, leading to the existence of a thickness window within which smooth metal films could be formed [15]. In the Ag/GaAs(1 1 0) system, the long-range forces drive all atoms in the Ag film involved in the rearrangement for an atomically flat film. In the present case, since such flat films could form at LT, a mass rearrangement of atoms is not necessary, and the long-range force could just stabilize the film and suppresses possible roughing when warming-up to RT.

4. Conclusion

The morphology evolution of the Al films grown on Si(1 1 1)-7 × 7 at LT has been studied. A characteristic thickness of 4 ML is identified, at which atomically flat film forms and exhibits remarkable stability due to the QWS formation. Our results explain why QWS could be observed only for the films with 4 ML Al and above in this system. The work opens a new avenue for quantum engineering of their physical properties by using quantum size effects in the flat thin films, as demonstrated by our recent work on the superconductivity transition temperature oscillation in the Pb thin films on Si prepared this way [16].

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