Eur. Phys. J. D **24**, 343–345 (2003)
DOI: 10.1140/epjd/e2003-00139-0

THE EUROPEAN PHYSICAL JOURNAL D

Buffer effects of titanium in the case of silver/$\alpha - Al_2O_3(0001)$

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Received 10 September 2002
Published online 3 July 2003 –

Abstract. The influence of thin titanium layers on the growth of silver clusters on $\alpha - Al_2O_3(0001)$ is investigated. We demonstrate through *in situ* RHEED measurements that titanium can relax stress in a growth mode where two lattice parameters show up simultaneously. Above a certain thickness, the lattice parameter closest to the bulk value of titanium dominates. Depending on the amount of stress in the titanium layer, silver films can either develop 3D textures or grow in epitaxy and form 2D like films.

PACS. 61.14.Hg Low-energy electron diffraction (LEED) and reflection high-energy electron diffraction (RHEED) – 68.35.-p Solid surfaces and solid-solid interfaces: Structure and energetics – 68.47.Jn Clusters on oxide surfaces

1 Introduction

Thin metallic films or clusters on oxides surfaces are often studied for their remarkable catalytic, optical and electronic properties. An important application of such systems is in low emissivity coatings on windows where a silver film improves the thermal insulation of the glass. Unfortunately, the low cohesion energy and adhesion of silver on most oxide surfaces makes its use in applications tedious. Different buffer layers can be applied to promote the adhesion properties. Titanium is known to be a very efficient buffer for many metal on oxide systems and this is often seen as the result of titanium's high free surface energy.

In previous papers, the buffer effect of titanium on silver was indirectly demonstrated through optical reflection *in situ* measurements of the silver plasmon [1]. It was found that the use of titanium buffers had a significant influence on the morphology of silver films, although the effect of the titanium film was shown to depend on its thickness. Very thin titanium layers (<0.3 nm) hardly produce any change in the three dimensional growth of silver – it remains as on the bare Al_2O_3 surface. In contrast, when deposited on a titanium layer of 0.6 nm silver shows a better wetting of the substrate. However for higher titanium coverage, the quality of the wetting decreases, although it remains better than on the bare surface. The complexity of this scenario can hardly be explained by the surface energy of titanium alone. To our knowledge, only a few studies deal with the crystal structure of the interface $Ti/Al_2O_3(0001)$ and the buffer effect of titanium on $Cu/Al_2O_3(0001)$, see [2,3]. In these papers a very thick titanium buffer (100 nm) layer is found to promote the epitaxy of Cu(111) and the epitaxial relations with the substrate were: $Ti(0001) \parallel Al_2O_3(0001)$, $Ti(1\bar{1}00) \parallel Al_2O_3(2\bar{1}\bar{1}0)$ and $Ti(2\bar{1}\bar{1}0) \parallel Al_2O_3(1\bar{1}00)$. This means that the hexagone of titanium rotates 30° with respect to the hexagone created by the outer Al atoms of $Al_2O_3(0001)$. The authors only investigated thick films and they did not observe stress relaxation in any of the layers.

Considering the above mentioned epitaxial relationships we can assume that Ag(111) is the most likely orientation on Ti(0001). It can be anticipated that the Ag/Ti epitaxy is favoured over the Ag/Al_2O_3 epitaxy because it corresponds to a lower mismatch (−1.76% *versus* 5.9%). Here we suppose a $Ti/Al_2O_3(0001)$ epitaxy despite a rather big mismatch (6.8%). In the present paper, we deal with the fundamental aspects of the growth and buffer effect of thin titanium layers on the growth of silver on $Al_2O_3(0001)$. We want to elucidate if thickness dependent stress relaxations in the Ti layer play a role on the morphology of silver films.

2 Surface preparation and experiments

Single crystalline $Al_2O_3(0001)$ substrates from Mateck were prepared using acetone plus ultrasonic bath followed by a cleaning in a 10 percent dilution of a standard buffered basic soap Alconaxs with PH = 10.6, then sample was washed in deionized water and dried in isopropanol vapor. Afterwards, an *ex situ* heat-treatment was done under 1 atm O_2 to 1320 K to obtain flat surfaces.

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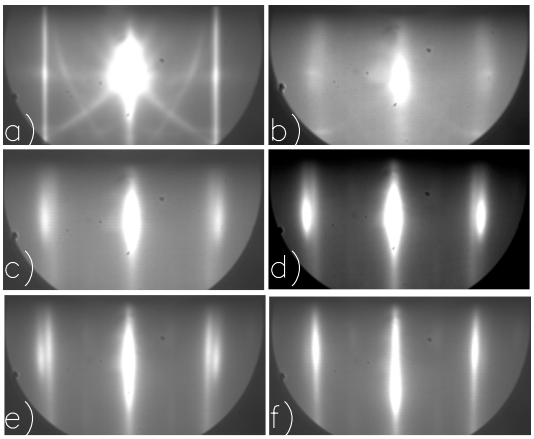

Fig. 1. RHEED images of titanium growth on $Al_2O_3(0001)$ ($[10\bar{1}0]$ axis): (a) bare substrate, (b) 0.6 nm, (c) 1.8 nm, (d) 3.9 nm, (e) 4.7 nm, (f) 6.0 nm.

The samples were transferred to a MBE installation and heated slowly to 820 K under partial pressure of 5×10^{-5} torr O_2 over a couple of hours in order to get rid of carbon contamination. Then the samples were heated to 1070 K for 30 minutes and cooled under oxygen before transfer to the evaporation chamber.

Titanium and silver films were evaporated on the samples using an Telemark electron gun. The flux was between 0.08–0.1 nm per min and the samples were held at 400 K and the chamber pressure was below 10^{-9} torr. To eliminate any distortions of the diffraction pattern due to stray fields from the electron guns, special care was taken to align the optical center of the RHEED with the electron guns in operation condition. The evolution of the growth was followed by a Staib RHEED instrument and the diffraction patterns were recorded using a CCD camera. During the deposition any movement of the samples used for relaxation measurements were avoided to keep the substrate reference for the diffraction patterns. Several films of titanium were grown and silver was deposited for different thicknesses of the titanium layer. Other samples were prepared to determine the epitaxial relations between titanium and the Al_2O_3 substrate.

3 Growth of the titanium film

Figure 1 shows the typical evolution of a titanium layer. The film starts growing with a lattice parameter close to the substrate lattice l_0 but the diffraction rods are broad and not very intense – an indication of a low degree of order in the growing film. When the titanium coverage increases the diffraction pattern gains intensity. Within a broad range of titanium coverage, two separated lattice parameters l_1 and l_2 coexist. At lower coverage, the external rod l_1 is the most intense (Figs. 1c and 1d). For increasing coverage the internal rod l_2 increases in intensity to finally dominate the pattern (Fig. 1f). This phenomenon persist over a few nms then the evolution stops and the position of the rods does not change (we tested this till

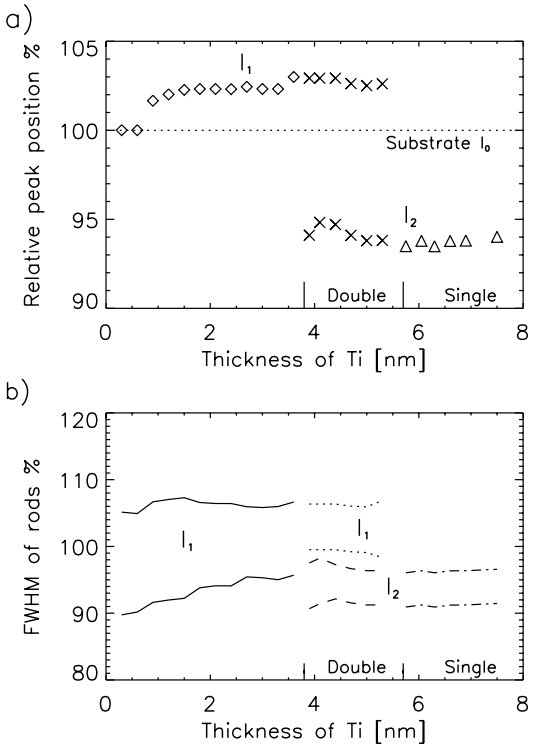

Fig. 2. Evolution of the distance between the lattice rods with respect to the substrate for the whole growth process shown in Figure 1. (a) Reciprocal lattice parameters l_0, l_1 and l_2, see text for definition. (b) Width of the diffraction rods illustrating the peak splitting observed between 4 and 6 nm of titanium deposition.

20 nm of titanium). Note that the thickness at which this occurs depends on the sample and sample preparation.

In order to analyse the data in detail, we have extracted the position of the rods with respect to the substrate lattice. To get a high precision on the measurements, we summed three photos taken for each film thickness. After that, we have cumulated data along the diffraction rods to obtain profiles with the high contrast. Both the position and the full width half maximum (FWHM) of the diffraction rods were measured. The results are represented in Figures 2 and 3. As the surface lattice of the alumina crystal might differ from that of the bulk, the data is presented in percentage of the reciprocal substrate distance.

Figure 2 shows that titanium first grows with a lattice constant close to that of the substrate l_0 and then undergoes a slight contraction of 2% to a lattice constant l_1. This is surprising since titanium is already in contraction on the substrate there should be no gain in energy by a further contraction. The lattice constant l_2 corresponds to a lattice parameter which is around 6.3% larger than that of the substrate and very close to the bulk value of titanium and silver. It becomes the only lattice rod at 5.8 nm. The FWHM data (Fig. 2b) indicates that the diffraction rods are rather blurred during the first part of the growth. The rods narrow as the film relaxes. Figure 3 shows that the peak around l_1 is asymmetric and has a skewness

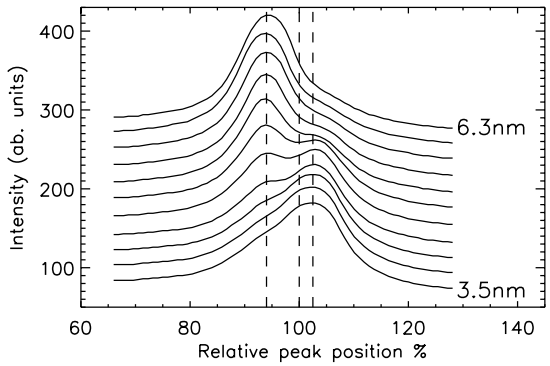

Fig. 3. Evolution of the peak profile for various Ti film thickness ranging from 3.4 nm to 8.5 nm. On the abscissa relative peak position in reciprocal space where 100% corresponds to the position of the initial substrate peak l_0. The two other dashed lines indicate the positions of the two peaks l_1 and l_2 appearing during titanium deposition.

towards higher lattice spacings. This indicates that there is a disorder in the film, but also that it is likely that the lattice parameter l_2 is already present even at the earliest stage of the growth.

4 Growth of silver on the titanium buffer layer

Films of 2 nm of silver were grown without or with titanium buffers of different thickness. Figure 4 shows typical RHEED patterns of the silver films. The system Ag/$Al_2O_3(0001)$ grows without any epitaxial relation and develops the ring structure typical for poly-crystalline 3D films. When a thin titanium layer is present (Fig. 4) the silver film grows with a texture around the sixfold symmetry of the Ag(111). On a titanium buffer where both spacing l_1 and l_2 are present the silver film develops a complex 3D texture (Fig. 4b). If the titanium has relaxed, so that only the spacing l_2 is left, the silver grows without any loss of intensity or broadening of the rods – a signature of a very good epitaxy and a 2D-like morphology.

5 Discussion

Some groups [2,3] have examined the buffer effect of titanium in the case $Cu/Al_2O_3(0001)$. However these studies mainly dealt with very thick buffer films (100 nm) and only reported epitaxial 2D like growth of titanium with conservation of the Al_2O_3 lattice parameter. No stress relaxation was observed in the titanium.

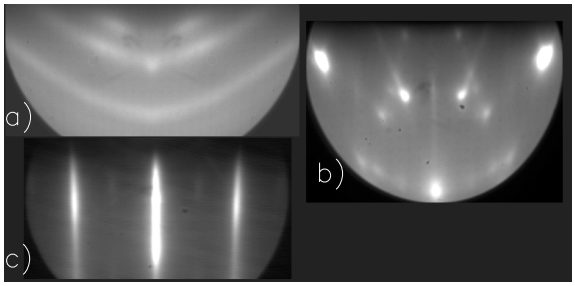

Fig. 4. RHEED patterns of 2 nm silver on different titanium layers. (a) Silver on bare aluminia silver is poly-crystalline, (b) for 4 nm titanium a 3D texture develops, (c) for a 6 nm thick relaxed titanium layer an almost 2 dimensional epitaxial growth occurs.

Previous results have demonstrated that the titanium buffer must be thick enough to be metallic to promote the wetting of the alumina substrate by silver [1]. Present data show that the way in which titanium affects the crystallinity and morphology of the silver layers depends on its thickness. This buffer effect seems to be linked to elastic relaxations within the titanium film but its influence on silver is not simple. The silver film does not rigidly adapt the titanium lattice and exhibits a remarkable amount of different textures. Epitaxy is only obtained when the lattice constant is very close to the silver bulk value. The various structures observed for the silver films still remain to be fully characterized and need to be clearly linked to the stress in the buffer. Moreover, the mechanisms behind the growth of titanium on Al_2O_3 remain to be understood. We plan to deal with this subject in future studies.

We wish to thank the group of Dr. Claude Fermon at CEA-France for the use of their RHEED/UHV facility.

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