

Two dimensional Si layer epitaxied on $\text{LaAlO}_3(111)$ substrate: RHEED and XPS investigations

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Abstract. We report the epitaxial growth of one Silicon monolayer on the $\text{LaAlO}_3(111)$ substrate, a high- κ crystalline oxide. Structural and chemical properties were investigated in-situ using reflection high energy electron diffraction (RHEED) and X-ray photoelectron spectroscopy (XPS). The deposition was achieved by molecular beam epitaxy in the temperature range RT-500°C. A two-dimensional epitaxial growth mode is observed for a deposition at temperature between 300°C and 500°C. The deposited single layer is formed by two dimensional (2D) structures of Si.

1. Introduction

Dimensionality is one of the most important parameters which can exhibit dramatically different properties, depending on its crystal structure arrangement in a 0, 1, 2 or 3 dimensional (D) [1]. Currently there is an increasing interest in two-dimensional conducting materials such as graphene, a two-dimensional honeycomb lattice of carbon atoms [2]. Since the discovery of graphene and the important advancements in this research field [3], strong efforts have been investigated on graphene like materials (theoretically and experimentally), especially on silicon [4]. Silicene, the considered equivalent of graphene for silicon [5] forming a new synthetic atomic-thin two dimensional hexagonal silicon allotrope, has recently generated a very strong interest. It was first synthesized by silicon deposition on silver (110) and (111) [6, 7, 8, 9, 10]. While silicon is right below carbon in the periodic table of elements, valence orbitals do not sp^2 hybridize as easily as for its smaller counterpart [11]. Also it is difficult to form a freestanding 2D layer. Nevertheless, recently a theoretical study predict a possible approach to grow these graphite-like nanolattice by using a self-assembled layer-by layer growth method [12]. Furthermore Fleurence et al. demonstrated the successful growth of epitaxial silicene on a diboride surface [11].

Our group began studying silicon adsorption on lanthanum aluminate LaAlO_3 (LAO) surfaces a high- κ crystalline oxide several years ago. LAO is a highly attractive material due to its promising properties, including high value of dielectric constant (24), good thermodynamic stability with respect to Si [13, 14] and large band offsets (>2 eV) with Si [15, 16]. Indeed the growth of organized layer of silicon is expected, because on one hand the lattice mismatch



between silicon and LAO(100) is of only about 1% when the Si lattice is rotated by 45° around an axis perpendicular to the surface with respect to the LAO lattice, on the other hand no interdiffusion was observed between silicon and LAO [17].

In this paper we have studied the growth of one silicon monolayer deposited by molecular beam epitaxy (MBE) on a LAO(111)- $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ reconstructed surface, at different substrate temperatures. In the ($300^\circ C$, $500^\circ C$) temperature range a two dimensional epitaxial silicon structure has been successfully obtained on the LAO(111) surface.

2. Experiments

The experiments were performed in an a custom-built ultra-high vacuum (UHV) system with a base pressure of about $P = 10^{-10} mbar$, equipped with in-situ crystallographic and chemical characterization techniques such as reflection high-energy electron diffraction (RHEED) and X-ray photoelectron spectroscopy (XPS). LAO(111) substrates were purchased from CrysTec GmbH. After an ex-situ treatment in organic solvent, the LAO(111) substrate was cleaned in-situ with a heating during one hour at $900^\circ C$ in order to obtain the $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ reconstruction, the signature of a clean surface. The substrate temperature was controlled with an optical pyrometer. During the annealing, the pressure was maintained lower than $P = 10^{-9} mbar$. To evaporate Si, an electron gun was used. The deposition rate is about 0.25 monolayer/min and was controlled with a quartz microbalance. One monolayer (ML) is defined as the ideal atomic density in a Si (111) plane, i.e. $P = 7.8 \cdot 10^{14} at./cm^2$. The thicknesses indicated in this article were determined from the growth time assuming constant deposition rate. Both LAO(111) surface and Si growth were monitored in real time with a Staib Instrument RHEED system operating at an accelerating voltage of 25kV. XPS spectra were carried out using an hemispherical photoelectron spectrometer (Omicron EA 125) and a conventional AlK α ($h\nu = 1486.6$ eV) photon source (Omicron DAR 400). The electron acceptance angle is about $\pm 8^\circ$ and the analysis area (diameter) does not exceed 1.5 mm. XPS chemical species core levels are analysed with pass energy of 20 eV. An overall resolution of ~ 1 eV for Ag $3d_{5/2}$ at 885.5 eV was used as an external reference. Binding energy shifts due to charge effects, was compensated by setting La $4d_{3/2}$ peak at 106.6 eV. In order to have a surface sensitive analysis geometry, the polar angle between the spectrometer and the normal of the surface is fixed at 50° . Core level spectra were fitted using CasaXPS software version 2.3.15 with symmetric mixed Gaussian-Lorentzian components.

3. Results and discussion

Figure 1 shows the RHEED evolution along the $\langle 11\bar{2} \rangle$ (figures 1(a)-(c)) and the $\langle 1\bar{1}0 \rangle$ (figures 1(d)-(f)) azimuths, of 1 ML Si deposit as a function of deposition temperature. The presence of Kikuchi lines on the RHEED patterns reveal the excellent flatness of the surface. Starting from a streaky diagram corresponding to a clean and flat LAO(111) surface (figures 1(a),(d)), we observe an intensity attenuation of integral and fractional streaks after the deposit of 1 ML Si at $300^\circ C$ (figures 1(b),(e)) and $500^\circ C$ (figures 1(c),(f)), but the integral streaks are still visible on the RHEED patterns along $\langle 1\bar{1}0 \rangle$ and $\langle 11\bar{2} \rangle$ azimuths. The persistence of the integral streaks related to LAO(111) surface asserts that the growth is epitaxial and 2D. The system does not follow the thermodynamic predictions which consist in an immediate 3D growth mode. The single layer deposit on LAO(111) maintained at high temperatures ($300^\circ C$ and $500^\circ C$) during the growth is a two dimensional (2D) structure of Si. It seems that the reconstruction will govern the orientation and the anchorage of the Si deposit because the $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ diffraction signature disappears immediately after the deposit begin. Nevertheless, as the theoretical model of the $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ surface reconstruction is never precisely depicted in the literature, it is not possible to propose an atomic model of the relationship between the 2D Si layer and the LAO(111) surface.

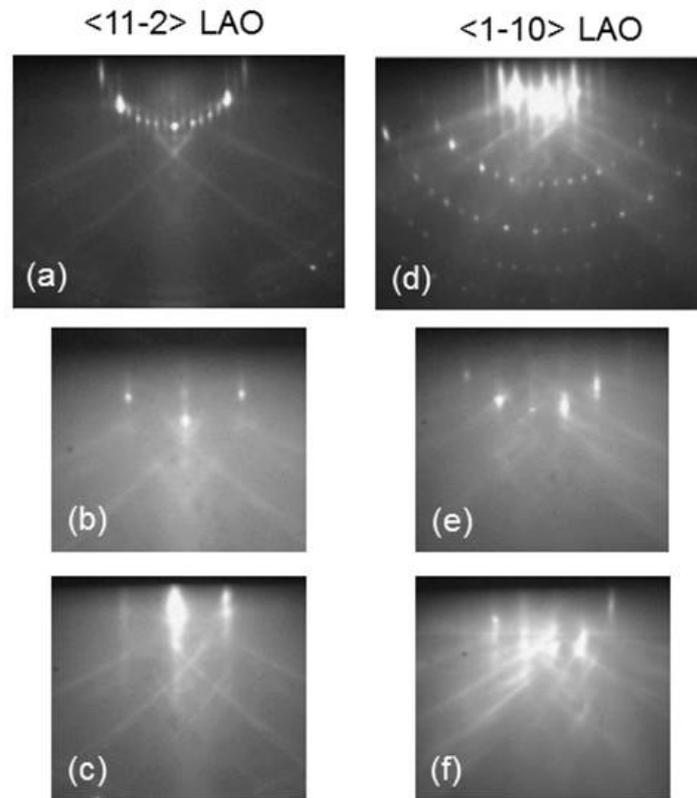


Figure 1. RHEED pattern evolution, along the $\langle 11\bar{2} \rangle$ azimuth (a-c) and $\langle 1\bar{1}0 \rangle$ azimuth (d-f) for the clean LaAlO_3 substrate ((a),(d)), after deposit at 300°C ((b),(e)) and 500°C ((c),(f)) of 1 ML Si.

In order to test the structural stability of the layer, the Si layer deposited at 500°C has been annealed at 600°C during 45 min (figure 2). The RHEED diagrams recorded after this thermal treatment along the $\langle 11\bar{2} \rangle$ azimuth and the $\langle 1\bar{1}0 \rangle$ azimuth are reported in figure 2(a) and 2(b) respectively. No drastic change has been pointed out on the diffraction patterns demonstrating a good thermal stability of the deposited 2D Si layer in spite of the thermodynamic predictions. It seems that the 2D Si layer is a new equilibrium shape on the $\text{LAO}(111)$ surface.

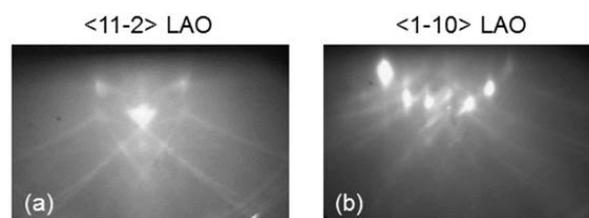


Figure 2. RHEED patterns after annealing at 600°C of the Si monolayer deposit at 500°C , along the $\langle 11\bar{2} \rangle$ (a) and $\langle 1\bar{1}0 \rangle$ (b) azimuths.

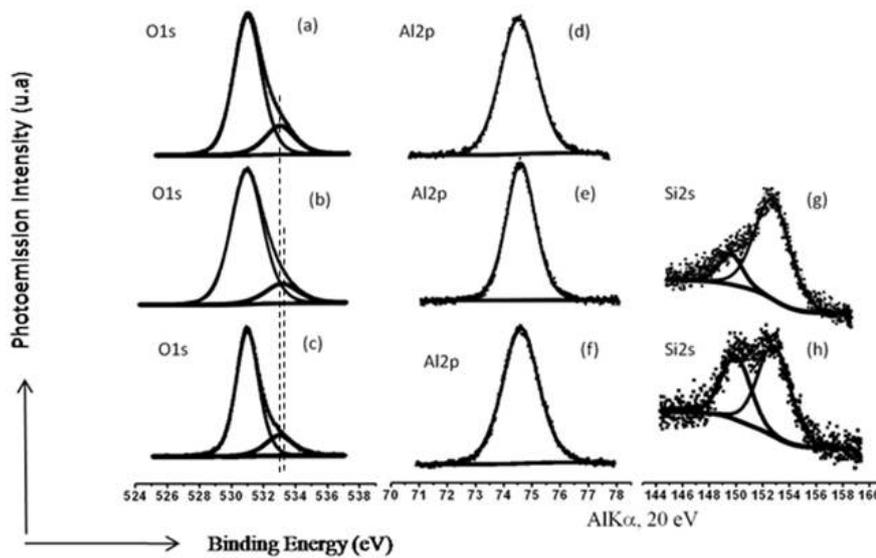


Figure 3. XPS O1s (a-c), Al2p (d-f) and Si2s (g,h) core level peak evolution as a function of the deposition temperature of 1ML of Si on LaAlO₃(111): for the clean substrate (a,d), at 300°C (b,e,g) and at 500°C (c,f,h).

In order to determine the chemical composition of the deposited silicon monolayer as well as the Si/LAO interface quality, XPS analyses have been performed. The Si2s core level has been chosen because the Si2p component is overlapped with La₄d_{5/2} one. Figure 3 displays the evolution of O1s, Al2p and Si2s core level spectra, recorded in the case of clean LAO substrate (a),(d) and after the deposition of 1 silicon ML at 300°C (b, e and g) and at 500°C (c, f and h). First a complete C desorption is confirmed on the survey spectra (not shown here) after the LAO cleaning process. The O1s peak represented in figure 3(a) is recorded on a clean substrate and presents two components separated of 2 eV. The most intense component located at 531.3eV corresponds to the O environment in the LAO substrate. The second one, which appears at 533.3 eV, seems to be a surface component indicating that O atoms are probably involved in the LAO(111)-(2√3 × 2√3)R30° surface reconstruction. Its energy position could be attributed to Al-O environment indicating that LAO(111) surface could be Al terminated. Nevertheless, the Al2p core level presented on figure 3(d) exhibits only one component corresponding to the Al environment in the LAO substrate. The Al oxidation on top of the LAO does not lead to detectable chemical shift (0.2 eV) with respect to our experimental resolution (1 eV) and probably appears in order to complete the AlO₂ octahedral blocks (AlO₆⁻) constituting the LAO substrate. Except for an intensity decrease of Al2p spectra, correlated to the amount of Si, neither the form nor the full width at half maximum (FWHM) are affected by the deposit (Figure 3(d)-(f)). These observations are extensible to the La₃d_{3/2} peaks (not shown here) indicating that no covalent bonds are formed during the Si deposition with these elements. Whatever the temperature used in this work, Si2s peak deconvolution reveals two components (Figure 3(g),(h)). While the less intense component, located at 150.5 eV, is attributed to Si – Si₄ environments of pure Si [18, 19], the second one is shifted on 2.7 eV on the high binding energy side leading to a Si – SiO₃ and/or Si – Si₃O environments [20] indicating the formation of Si-O covalent bonds. This bond formation is ascertained on the O1s spectra by the appearance of a new component located around 533 eV, characteristic of Si – O_x (Figure 3(b),(c)), which

replaces the surface component observed after cleaning and discussed before (Figure 3(a)). The position and the intensity of this component are highly connected to the x value explaining the slight difference observed as function of the deposit temperature.

The Si2s spectra of a Si single monolayer on a flat LAO(111) surface at 300°C (b,e,g) and at 500°C exhibit two components which have been previously discussed. The intensity of the $S_i - Si_4$ component increases with the temperature. These observations strengthen our hypothesis of a progressive formation of a Si crystalline 2D-plane on top of the LAO(111) substrate which cover a more important part of the surface at 500°C than at 300°C. At the same time, the intensity of the component related to the Si-O bonds decreases. The bonds between the Si layer and the LAO substrate, already observed on the O1s spectra (Figure 3(b),(c)), are confirmed. But at 500°C it seems that a larger part of the Si atoms are linked to other Si atoms and less to oxygen atoms as for 300°C. The Si plane is progressively formed by increasing the deposition temperature. Nevertheless, the component located on the high binding energy side is most intense than the component associated to the pure Si, ascertaining the presence of Si-O covalent bounds in order to maintain a 2D Si layer on top of the LAO(111) surface.

4. Conclusion

We have carried out a structural and chemical growth study of 1 ML of silicon on LaAlO₃ (111) surface. We have shown that depending on the LAO(111) substrate temperature during silicon growth, a two dimensional epitaxial structure is observed. The annealing at 600C of the single silicon monolayer deposit at 500°C does not promote the formation of 3D structures ascertaining the stability of the two dimensional deposit.

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