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Thickness-dependent evolution of structure, electronic structure, and metal-insulator transition in ultrathin $V_2O_3(0001)$ films on Ag(001)

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ABSTRACT

Epitaxial hexagonal $V_2O_3(0001)$ films were grown on cubic Ag(001) substrate for coverages ranging from 1-20 monolayers equivalent (MLE) and have studied their structure, electronic structure and the metal-insulator transition (MIT) using Low Energy Electron Diffraction (LEED), X-ray Photoelectron Spectroscopy (XPS) and Angle-Resolved Photoemission Spectroscopy (ARPES) techniques. Detailed LEED and XPS study reveal that, for the lower film coverages (~1 MLE), a complex (coexisting phase of) vanadium oxide is formed while from 3 MLE coverage onwards, three-dimensional crystallites of V_2O_3 grows epitaxially. Our LEED results also show that the hexagonal surface of $V_2O_3(0001)$ is stabilizing on top of square symmetry substrate by the formation of twin-domain structure, where each domain is rotated by 90^o. Our photoemission results show that the surface of V_2O_3 is more insulating than its bulk, similar to the case of many strongly correlated oxide surfaces which is discussed based on the valence band electronic structure with varying probing depth. Evolution of the surface electronic structure was also studied as a function of the film thickness. Further, the effect of lattice strain, film thickness and the domain formation on the metal-insulator transition (MIT) are discussed. The change in the orbital occupancy of ($a_{1\ g}$, e_g^π) and (e_g^π, e_g^π) orbitals of V 3 *d*, a vanishing of quasiparticle (QP) peak and opening an energy gap at the Fermi level is observed below a critical temperature as a consequence of the MIT.

1. Introduction

Growth of ultrathin transition metal oxide films on metal substrates is of high scientific and technological interest as they show novel electronic and magnetic properties than their bulk counterparts. Study of the interface created between the metal substrate and oxide film is crucial as it plays a significant role in deciding the properties of the films such as the reactivity, catalytic activities *etc*. [1–3]. Among the transition metal oxides, the case of V_2O_3 is rather interesting as it displays a first-order metal-insulator transition (MIT) at 170 K with many orders of magnitude jump in the conductivity. Vanadium oxide shows a complex phase diagram due to the existence of multivalency of vanadium in different vanadium oxides. Depending upon different growth conditions and coverage, the formation of different composition [V^{2+} to V^{5+}] and structure of vanadium oxide have been reported. In particular, V_2O_3 is a well-known model system to study the strong electron-electron correlation effects [4]. V_2O_3 transforms its crystal structure from trigonal to the monoclinic, accompanied with a 1.4% of volume increase, favoring the Mott-Hubbard mechanism for the MIT. Mott-Hubbard systems, are the important class of materials, where strong electron correlations within the transition metal *d*-bands induce small changes in the electronic structure close to the Fermi energy which manifests as spectacular macroscopic effects such as metal-insulator transitions [5]. In these systems, the insulator to metal transition is characterized by a coherent quasiparticle peak (QP) developing between the incoherent Hubbard bands.

Most of the studies related to the electronic structure of the V_2O_3 systems are focused either on the single crystals or on the thick films. However, the evolution of the electronic structure and the effect of the MIT of V_2O_3 films in the ultrathin regime is not addressed so far. In fact, Luo et al. [6] has reported that for films below a critical thickness (~20 nm), the V_2O_3 films does not show any MIT. Thus, it is important to study the evolution of the electronic structure and MIT occurring in ultrathin V_2O_3 films. Although there are some experimental studies, still the detailed understanding of the growth processes of ultrathin V_2O_3 layers on metal surfaces is still poorly understood. The growth of oxide film on a metal surface is itself interesting as they show a strong interplay between the thermodynamic and kinetic effects, which determines the structure and properties of the film.

Thin films of V_2O_3 has been grown on metal surfaces, like Au(111), W(110), Rh(111), Pd(111) by different groups [7–9]. It is reported that oxide layers formed on the metal substrate have a lower oxidation state

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than the thermodynamically most stable phases [10]. Surnev et al. [9] have shown that for low film thicknesses (1-2 MLE), the formation of a mixed phase of vanadium oxide is favoured other than one particular oxide phase. They have also shown, below three monolayers coverage of vanadium oxide on Pd(111), a quasi-oscillatory behavior of the oxidation states of vanadium is observed using scanning tunneling microscopy (STM), LEED and first principle Density Functional Theory (DFT) calculations [9]. There are possibilities of observing new chemisorption phenomena when a mixed oxide phase exists in a film. In all these studies, they have observed a V_2O_3(0001) surface is stabilized on Au(111), W(110), Rh(111) and Pd(111) substrates, due to the close match of the lattice parameters and the symmetry with the substrate.

The MIT of the thin films were also found to crucially depends on the surface structure and terminations. Pfuner et al. [11] has grown a thin film of V_2O_3(0001) on Rh(111) substrate and has shown that the film shows MIT with temperature, but it strongly depends on the surface termination. They have also shown that $p(1 \times 1)$ V_2O_3(0001) surface with surface terminated by vanadyl (V=O) group shows strong MIT but the MIT is effectively screened for the oxygen-rich $(\sqrt{3} \times \sqrt{3})$ R30^o reconstructed surface.

It is known that the hexagonal surface of V_2O_3 is the most stable surface. Then, it will be curious to ask how does the V_2O_3 film grows on a square symmetry surface? If the V_2O_3(0001) surface stabilizes on a (001) surface, then it will be interesting to study how does the nature of a square symmetry substrate supports the formation of a hexagonal symmetry film and what will be its effects on the structure, electronic structure as well as on the MIT of the V_2O_3(0001) film. Only a few studies have been performed on the growth of V_2O_3 films on (001) type substrates. Kishi et al. [12,13] have studied the growth of vanadium oxide layers on Cu(100) surface. From the XPS and LEED study, they have concluded that VO(111)-like hexagonal surface could be formed on Cu(100) and the thicker film may also contain V_2O_3 layers and islands. However, the detailed mechanism of the surface stabilization of V_2O_3 layers on square symmetry substrates is far from being understood.

In the present work, in order to address these various issues, we have performed the growth of ultrathin V_2O_3 films on Ag(001) substrate. The Ag(001) substrate has the square symmetry surface while the V_2O_3 is shown to grow in the hexagonal symmetry with (0001) stacking. We have studied the detailed surface structure, electronic structure and the MIT of these films using LEED, XPS and ARPES techniques as a function of the film coverages from 1 to 20 MLE. It should also be pointed out that there are no reports available on the growth of vanadium oxides on Ag(001) in the literature. Here, we have shown that the stability of hexagonal V_2O_3(0001) surface on the cubic substrate Ag(001) is provided by the formation of the twin domain structure. There exists a large misfit strain between the V_2O_3 film and the Ag(001) surface, resulting in the formation of the multi-domain twin structure as it occurs in thin films to minimize the electrostatic and strain energies in the films [14]. It is known that the presence of multi-domain structures in thin films generally has a profound impact on the properties of films *viz.* dielectric, piezoelectric and optical properties [15]. It is also seen that in addition to the multi-domain formation, strain relaxation also occurs by the formation of misfit dislocations. It will be interesting to explore the role of multi-domain structures on the MIT of these ultrathin V_2O_3 films.

Here, the thickness dependent evolution of the valence band and core level electronic structure of the V_2O_3 films has been studied in details. We observe the surface of the film is more insulating than the bulk due to the enhanced electron correlation effects at the surface. On the other hand, the metallic phase of strongly correlated Mott-Hubbard system is characterized by the observation of quasiparticle(QP) peak which is found to be very sensitive to the probing depth and has been discussed. We further show that film thickness and strain in the film plays a crucial role in the valence band electronic structure and the metal to insulator transition (MIT) of V_2O_3 film, while the domain structure does not affect the electronic structure. The change in the occupation of the ($a_{1\,g}$, e_g^π) and (e_g^π, e_g^π) orbital of V 3d have been observed below a critical temperature as a consequence of the MIT.

2. Experimental details

The Ag(001) substrate was cleaned by repeated cycles of Ar^+ ion sputtering (600 eV, 1 μA) for 15 min followed by annealing at 823 K for 20 min until a sharp $p(1 \times 1)$ LEED pattern was observed. The substrate preparation, growth and LEED measurements were performed in the preparation chamber with a base pressure of 1×10^{-10} mbar. Vanadium was evaporated from a well-degassed water-cooled e-beam evaporator at a constant rate of 0.3 Å/min in oxygen partial pressure of $p(O_2)=2\times10^{-7}$ mbar for the deposition of the V_2O_3 film on Ag(001) substrate, while during deposition, the substrate was kept at 473 K. The rate of V-deposition was calibrated with a water-cooled quartz crystal thickness monitor, mounted on a linear drive which was moved to the sample position for the rate measurements. One monolayer equivalent (MLE) of vanadium oxide film is defined as the atomic density corresponding to 1 ML vanadium on Ag(001), i.e., 1.75×10^{19} atoms/m^2, under oxygen atmosphere. After deposition, the film was annealed at 673 K for 10 min in ultra high vacuum (UHV), following the standard growth procedure of the V_2O_3 films [11]. The sample temperature was measured by a K-type thermocouple, in contact with the Ag crystal. The crystalline quality of the film and the symmetry directions were determined by a four-grid LEED apparatus while a highly-sensitive Peltier-cooled 12-bit CCD camera was used to collect the LEED images. Photoemission spectroscopic measurements like XPS and ARPES were performed in analysis chamber having a base pressure better than 8×10^{-11} mbar. ARPES experiments were performed using a combination of VG SCIENTA-R4000WAL electron energy analyzer with a 2D-CCD detector and a high flux GAMMADATA VUV He lamp attached to a VUV monochromator, which has been described in detail elsewhere [16]. The ARPES measurements were performed using monochromatized ultraviolet He I$_\alpha$(21.2 eV) and He II$_\alpha$ (40.8 eV) resonance lines, while the XPS measurements were performed with Al K$_\alpha$ monochromatic X-ray source (1486.6 eV) from VG SCIENTA. The position of the Fermi energy (E_F) was determined from a clean polycrystalline Ag sample. We have taken narrow energy scans close to E_F and have fitted the spectrum with the Fermi-Dirac function convoluted with the resolution function to obtain the Fermi energy position as well as to estimate the total experimental energy resolution. At room temperature (RT) we estimate a total experimental energy resolution of about 100 meV for the UPS (using He I$_\alpha$ and He II$_\alpha$ photons) while for the monochromatic XPS we have set the energy resolution to about 600 meV. The angular resolution of the analyser with the wide angle lens mode used was better than 1 degree. All the binding energies used here are relative to the E_F position, i.e., (E-E_F). The XPS spectra were fitted with a Shirley-type background as well as with Gaussian-Lorentzian (GL) peak shapes using CasaXPS package. All measurements, except in the MIT section, have been performed at RT.

3. Experimental results and discussions

3.1. Core level electronic structure of V_xO_y: XPS study

There is a high possibility that the grown vanadium oxide film may contain more than one oxidation state of vanadium due to its multivalent character. XPS measurements have been carried out in order to probe the exact phase of vanadium oxide of the film as well as to study the evolution of the core level electronic structure with film thickness. Fig. 1(a) shows the core level spectrum of both V 2p and O 1s for different film thickness, as they appear very close in binding energy. For the case of lower film thickness (1 and 3 MLE), as the intensity of