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Structural and electronic properties of V/Ag(0 0 1) films: Effects of substrate temperature and film thickness

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ABSTRACT

The growth mode, structural and electronic properties of vanadium films on Ag(0 0 1) were investigated using low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS) and angle-resolved photoemission spectroscopy (ARPES) techniques. Previously, it was believed that the layer-by-layer growth of vanadium films is possible (for the first 3–4 layers) at the substrate temperature range of 373–428 K, while our results suggest, vanadium prefers to grow in a three-dimensional (3D) island form and Ag segregates on top of vanadium islands. Detailed band dispersion mapping along the high symmetry directions of V(0 0 1) surface Brillouin zone (SBZ) clearly shows the presence of quantum-well states (QWS) along with the desired bands of V(0 0 1) surface, due to the formation of Ag/V/Ag(0 0 1)-like structure. At different growth temperatures, a substantial change in the valence band electronic structures are also observed due to the appearance of *sp* and *d* derived Ag QWS, spreading all over the valence band, originating from the different island height of the segregated Ag layers. QWS are absent for the low temperature (~108 K) grown films, indicating the absence of Ag-segregation. Furthermore, we compare our band dispersion data with the available theoretical calculations and good agreement between them is observed. Moreover, our results can be a valuable resource for some future research of noble metal-transition metal interfaces in particular in understanding a complexity of the valence band spectra. These results will also help to explain why contradictory results are reported in the literature on monolayer magnetism of V/Ag(0 0 1) system.

1. Introduction

Bimetallic surfaces possess novel chemical and physical properties and consequently have been studied extensively over the last three decades [1,2]. In particular, transition metal overlayers on metallic substrates are of great scientific interest because of their diverse tunability of the magnetic and electronic properties. Theoretical calculations have addressed an interesting issue: the possible existence of magnetic ordering at the surfaces of a nonmagnetic bulk material [3]. In bulk body-centered cubic structure, vanadium is nonmagnetic, although as a single atom it shows a magnetic moment of $3\mu_B$ in the ground state. Moruzzi et al. [3] has theoretically shown the volume dependence of transition-metal magnetism using first-principles band theory. The transition metal, manganese, is paramagnetic in the bulk crystalline form while its monolayer shows antiferromagnetism when it grew on Ag(0 0 1) substrate [4]. In the case of thin-films, the enhancement of magnetic moment and perpendicular anisotropy are very interesting in view of the possible applications in magneto-optic high density storage media [5]. Experimentally, the appearance of magnetic moments in vanadium films has been reported when it is deposited on a ferromagnetic substrate (e.g., Fe(1 0 0)), originating from the direct exchange interaction [5]. Rau et al. [6] have performed electron capture spectroscopic study on V films on Ag(1 0 0) where they observed ferromagnetic behavior with a thickness dependent Curie temperature. On the other hand, spin-resolved photoemission spectroscopy (SRPES) [7] and magneto-optic Kerr effect (MOKE) [8] measurements do not show any evidence of ferromagnetism in a V monolayer on Ag(0 0 1). Further, Blügel et al. [9] have theoretically shown that the ground state of monolayer V on Ag(0 0 1) is antiferromagnetic. In general, the understanding of the magnetic state of vanadium in ultrathin film systems with reduced coordination number is rather controversial [6–12].

In the form of single-crystalline thin film, growth of vanadium on Pt (111) [13], Ag(0 0 1) [6–8], Fe(0 0 1) [14], Cu(0 0 1) [15] and TiO_2(110) [16] substrates are reported. Vanadium films deposited on TiO_2(110) surface shows growth of vanadium islands with a bcc structure having no long-range coherence. Reported LEED and Auger electron spectroscopy (AES) studies [6–8] shows that V grows on Ag (0 0 1) as uniform layers (for the first 3–4 layers), and does not exhibit

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significant three-dimensional (3D) island formation, at least below five layers in the temperature range of 373–428 K. However, according to the equilibrium thermodynamics, as the surface energy of vanadium ($3\,J/m^2$) is more than twice the surface energy of silver ($1.2\,J/m^2$) [8], intermixing at the interface is not likely, but cluster formation or Ag segregation, rather than layer-by-layer growth is favoured for the V/Ag (0 0 1) system. The lack of layer-by-layer growth and Ag segregation is reported for the similar system, V/Cu(0 0 1) [17]. Ag segregation is also reported for the other transition metal systems like, Cr/Ag(0 0 1) [18] and Mn/Ag(0 0 1) [19]. Electronic band structure measurements can give some insight about the Ag segregation/island formation in the film, as previous growth study of Ag films on V(0 0 1) has shown that Ag quantum- well states (QWS) are formed due to the electron confinement within the Δ_1 gap of vanadium [20]. Thus, for the Ag-segregation on V(0 0 1) film, one should expect the presence of QWS in the valence band electronic structure and in the case of 3D island growth, a bulk-like electronic structure is expected even for the lower film coverages. Although, most of the studies on the vanadium system have been devoted to the understanding of the magnetism, however till date the magnetic state of V(0 0 1) surface is not established. Despite the persistent interest in the magnetic properties of ultrathin vanadium films, only a few papers deal with their electronic properties [21,22]. To our knowledge, in the case of thin-film, a complete valence band mapping along the high symmetry directions of the V(0 0 1) SBZ are still missing in the literature. However, a detailed knowledge of the band structure, the electronic density of states and possible surface-induced band narrowing is essential for the understanding of surface magnetism and complex electronic structure of noble metal-transition metal interfaces.

In this paper, we have grown vanadium films of different thickness on Ag(0 0 1) substrate, kept at temperatures ranging from 108 to 473 K and investigated their surface and electronic properties using LEED, XPS, and ARPES techniques. Our results show the signature of Ag-segregation on top of the three-dimensional V(0 0 1) islands in the temperature range of 373–428 K, while previously it was believed that flat layer growth is possible in this temperature range [6–8]. Further, ARPES results directly show the presence of QWS in the film due to the formation of Ag/V/Ag(0 0 1)-like structure in the temperature range of 373–428 K. At different growth temperatures, substantial changes in the valence band electronic structure are also observed due to the appearance of QWS from the different island height of the segregated Ag layers. The effective mass of the electrons in the QWS are extracted from the ARPES data which is matching well with the previously reported Ag QWS on V(0 0 1) substrate. The 108 K grown film does not show any such QWS, ruling out the possibility of Ag-segregation at low temperature deposition of vanadium films. Moreover, we show that the growth of flat-layer V films with long-range atomic order cannot be stabilized on Ag(0 0 1). Our result also suggests, the absence of flat layer growth could be a reason for the ambiguity between theoretical and experimental results on the monolayer magnetism of vanadium films on Ag(0 0 1), as flat layer growth of vanadium layer was considered for the theoretical study, while which is not feasible experimentally.

2. Experimental details

Epitaxial Vanadium films were grown on Ag(0 0 1) single crystal substrate, prepared by standard cycles of Ar^+ ion sputtering (600 eV, 1 μA) for 15 min, followed by UHV annealing at 823 K for 30 min until a sharp (1 × 1) LEED pattern was observed. The substrate preparation, growth and LEED measurements were performed in the preparation chamber with a base pressure of 9×10^{-11} mbar. High purity vanadium (99.95%) was evaporated from a well-degassed water cooled e-beam evaporator at a constant rate of 0.2 ML/min, while the substrate was kept at 108–473 K. During deposition of vanadium films, the chamber pressure was 2×10^{-10} mbar. 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 rate measurements prior to deposition. A monolayer (ML) is defined as an atomic density of vanadium, corresponding to that of the Ag(0 0 1) surface, *i.e.*, 1.75×10^{19} V-atoms/m^2 (surface atomic density of Ag (0 0 1) is 1.21×10^{19} Ag-atoms/m^2). The crystalline quality of the film was determined using a four-grid LEED apparatus (OCI Vacuum Microengineering). ARPES measurements were performed *in-situ* in the analysis chamber with a base pressure better than 8×10^{-11} mbar and attached to the preparation (growth) chamber. ARPES experiments were performed using a combination of VGScienta-R4000WAL electron energy analyzer with 2D-CCD detector and a high flux Gammadata VUV He-lamp attached with a VUV monochromator, which has been described in detail elsewhere [23]. We have used He I_α (21.2 eV) resonance line for the ARPES measurements, while the Al K_α monochromatic X-ray source (1486.6 eV) from VG SCIENTA was used for XPS measurements. The total experimental energy resolution for XPS and ARPES measurements was about 0.6 and 0.1 eV, respectively, including the thermal broadening near E_F at room temperature.

3. Experimental results and discussions

3.1. Structural analysis of V/Ag(0 0 1): LEED study

The face-centered cubic (fcc) Ag has a lattice parameter of 4.09 Å whereas the V has body-centered cubic (bcc) structure with a lattice parameter of 3.03 Å. As $\sqrt{2}$ times vanadium lattice parameter is 4.28 Å, so epitaxial growth of vanadium on Ag is possible with a 4.8% strain. By accommodating this strain, vanadium overlayer may form pseudomorphic overlayer on Ag(0 0 1) with its crystallographic ⟨100⟩ direction rotated 45° with respect to Ag. To understand the effect of substrate temperature and film thickness on the surface structure of vanadium films, different coverages of vanadium films have been grown at different substrate temperatures and studied their surface structure using LEED. Fig. 1(a)–(o) shows the evolution of the LEED pattern with film thickness and substrate temperatures, 108 K, 300 K and 428 K. All the images show (1 × 1) LEED pattern, ensuring the formation of epitaxial vanadium films on Ag(0 0 1). Images are shown at 36 eV and 56 eV incident electron beam energy. At 36 eV and 56 eV electron beam energy, the first-order diffraction spots originating from V(0 0 1) and Ag (0 0 1) surfaces, respectively, show maximum intensity. From Fig. 1(d)–(f), it can be seen that at 36 eV incident energy, 1 ML vanadium films show well-ordered $p(1 \times 1)$ structure and which is barely depends on growth temperatures, 108–428 K. However at 56 eV incident energy, LEED spots for the 108 K grown film shows 'halo' structure surrounded by each spot [see Fig. 1(a)]. This 'halo' structure is decreasing with the higher temperature growth and almost vanishes for the 428 K grown film [see Fig. 1(c)]. This can be seen more clearly from the radial profile plot of LEED spots (see Fig. 2(a)). Where the sharpness of the average radial profile plot gives information about the structural quality of the film. From Fig. 2(a) it is clear that the FWHM of the peak is lower for the 428 K grown film than the 300 K and 108 K, indicating the reduction of 'halo' structure and improvement of structural quality of the films with increasing temperature. These 'halo's, whose presence depends on the electron incident energies, reflect constructive or destructive interference between V islands in the coherence area and indicate that the surface is rough [24]. This also suggests, before completing the first atomic layer, a substantial amount of the V atoms occupy to the second layer. Very similar LEED pattern has been reported for the growth of Cr on Ag(0 0 1) at low temperature, originating due to the formation of rough Cr surface [25]. The film grown at 428 K (1 ML) does not show any 'halo's at whatever incident energy, suggest the growth of much larger V islands. However, whether these islands are 2D or 3D character cannot be concluded only by looking at the LEED images. With increasing film coverages to 2 ML, LEED quality changes drastically and high background to spot ratio is observed for all substrate temperatures between 108 and 428 K (not shown here). The 5

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