

Hydroxylated α -Al₂O₃ (0001) surfaces and metal/ α -Al₂O₃ (0001) interfaces

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Abstract

X-ray photoelectron spectroscopy was applied to study the hydroxylation of α -Al₂O₃ (0001) surfaces and the stability of surface OH groups. The evolution of interfacial chemistry of the α -Al₂O₃ (0001) surfaces and metal/ α -Al₂O₃ (0001) interfaces are well illustrated via modifications of the surface O1s spectra. Clean hydroxylated surfaces are obtained through water- and oxygen plasma treatment at room temperature. The surface OH groups of the hydroxylated surface are very sensitive to electron beam illumination, Ar⁺ sputtering, UHV heating, and adsorption of reactive metals. The transformation of a hydroxylated surface to an Al-terminated surface occurs by high temperature annealing or Al deposition.

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1. Introduction

Metal film growth and the formation of well defined interfaces depend sensitively on the crystallographic and electronic structure of the substrate surface. Alumina surfaces are one of the most extensively studied surfaces [1,2]. They are very important as thin-film substrates and catalyst supports. In particular, the crystallographic simple and energetically stable (0001) surface of corundum alumina (α -Al₂O₃; sapphire) offers a good playground for fundamental studies concerning the influence of surface properties (e.g., crystallographic- and electronic structure) on the formation of interfaces.

The unit cell of bulk α -Al₂O₃ can be described as a hexagonal unit cell containing six formula units of Al₂O₃ [3].

This unit cell consists of six close-packed hexagonal O layers. Al layers, which are not coplanar but buckled, are placed between these O layers. The Al ions are placed in 2/3 of the octahedral vacancies. All the ions are stacked along the *c*-axis of the unit cell in a sequence R-AlAlO₃-R (R: continuing sequence in the bulk). For bulk truncated α -Al₂O₃ (0001) surfaces there exist, from a geometrical standpoint, three different terminations (e.g., see Fig. 1 in Ref. 4): O layer termination (O₃AlAl-R), single Al layer termination (AlO₃Al-R), and double Al layer termination (AlAlO₃-R) [4–6]. The 3 surfaces possess different thermodynamic stabilities [6–10].

The O layer terminated surface has a large surface dipole moment and surface dangling bonds. Therefore, this surface is energetically unstable under almost all environmental conditions [6]. The O layer termination was observed experimentally only by Toofan and Watson who reported a mixture of 2:1 O/Al-terminated surface domains [11].

The single Al layer terminated surface is generally accepted to be the most stable unreconstructed α -Al₂O₃

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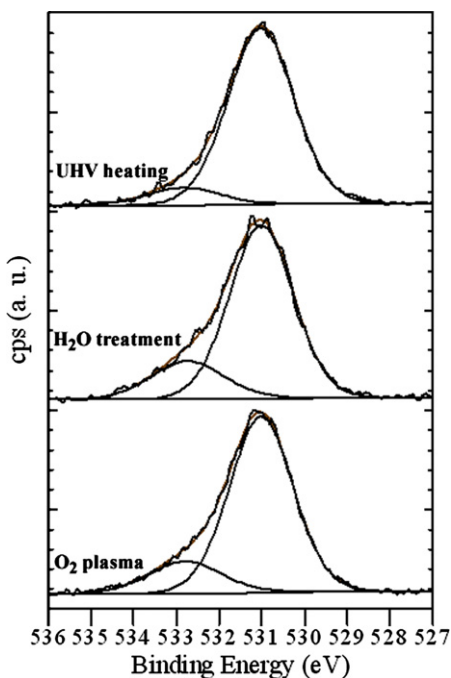


Fig. 1. O1s XPS spectra of the α -Al₂O₃ (0001) surface after UHV heating at 900 °C for 2 h, H₂O-, and O₂ plasma treatment at RT, respectively.

(0001) surface [4–19]. The surface is non-polar. Moreover, surface Al atoms strongly relax inward so that they are almost coplanar with respect to the second O layer. The relaxation is accompanied by a rehybridization of surface Al atoms to an sp² orbital configuration, which significantly stabilizes the surfaces via charge autocompensation [6]. The surface relaxation was calculated with density functional theory (DFT) to be about –85%, e.g., –85% [7], –82% [14,15], –87% [16], –86% [6,17], and –83% [19]. However, experimentally observed relaxations were smaller, ranging from –51% to –63% [4,5,13]. These results were obtained by X-ray diffraction (XRD) [5], low energy electron diffraction (LEED) [4], and ion scattering [13], respectively.

The (1 × 1) surface may be subjected to reconstructions in cases of O desorption or Al deposition onto the surface [20–24]. Such reconstructions are favored by energetical reasons. XRD and LEED investigations have revealed a ($\sqrt{31} \times \sqrt{31}$) R ± 9° reconstruction on α -Al₂O₃ (0001) surfaces heated in ultrahigh vacuum (UHV) at $T > 1200$ °C [21–23] or covered by Al [23,24]. The reconstructed surfaces were suggested to be terminated by a double Al layer, which contains hexagonal surface domains with Al (111) structure [20,21]. Such a structure has been directly imaged using dynamic-mode scanning force microscopy (SFM) by Barth and Reichling [20].

Hydroxylation of clean α -Al₂O₃ (0001) surfaces may result in further lowering of the energies of these surfaces [6–8,25]. Thus, the above O- and Al-terminated surfaces are expected to be reactive to water. Theoretically, *ab initio* calculation revealed that molecularly adsorbed water on Al-terminated surfaces is metastable and dissociates read-

ily. The H₂O dissociative reactions produce two types of surface OH groups: O_{ads}H and O_sH (O_{ads}: water oxygen; O_s: surface oxygen) [14,15,26]. Experiments confirmed the existence of OH-terminated α -Al₂O₃ (0001) surfaces by various techniques, e.g., SFM [20], XRD [27], thermal desorption [28,29], electron-energy loss spectroscopy (EELS) [30], and X-ray photoelectron spectroscopy (XPS) [31–36]. The surfaces in these studies were simply obtained via exposure to water or air.

As pointed out above, the α -Al₂O₃ (0001) surface exhibits four basic varieties of surface terminations, including O layer termination, single Al layer termination, double Al layer termination, and OH termination. Each of these surfaces has a unique stoichiometry, crystallographic and electronic structure, etc. The different surface terminations and properties deliberately depend on the surface treatment and can be manipulated by the surface preparation process. The different surface properties will significantly affect the formation of metal/alumina interfaces, for example, nucleation and growth of metal overlayers, interfacial bonding, and thus interfacial energy [32–43]. Among the different possible surfaces, the hydroxylated α -Al₂O₃ surface is of special importance. First of all, alumina surfaces are quite often covered by water or exposed, of course, to air during handling. Therefore, OH groups will always be present on the surfaces in case of no further special surface treatment. On the other hand, surface OH groups are critical for metal deposition. Hydroxylated surfaces are expected to exhibit higher reactivity to metals than clean Al-terminated surfaces [27,32–37]. Theoretical work [34,38] predicted that the reactions of Co and Cu with surface OH groups are exothermic. The interfacial reactions lead, instead of island growth, to the technologically important 2-D film growth and the oxidation of the metal in the initial stage of nucleation. In general, the strong interaction between metal adatoms and surface OH groups significantly changes the interfacial bonding and solid state wetting behavior [32–38]. Therefore, fully understanding and well controlling of the hydroxylated α -Al₂O₃ (0001) surface can contribute much to the elucidation of the nature of metal/alumina interfaces.

In the present paper, we concentrate on the hydroxylated sapphire (0001) surface (sapphire basal plane). Angle-resolved XPS was used to study the interfacial chemistry at the OH-terminated α -Al₂O₃ (0001) surfaces and interaction with various metals. In particular, we addressed the following points: preparation of the OH-terminated surfaces, the stability of the surface OH groups to different treatments, and the interaction between metal adatoms and OH groups. A critical comparison of our results to previous experimental and theoretical data will be given in Section 3.

2. Experimental

Single crystal α -Al₂O₃ (0001) platelets (10 mm × 10 mm × 0.5 mm, polished on one side, with a deliberate

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