Interaction of Water with Ordered $\theta$-Al$_2$O$_3$ Ultra Thin Films Grown on NiAl(100)

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Introduction

Metal oxide surfaces have been extensively studied due to their relevance to a vast number of materials engineering and catalytic process applications. In particular, Al$_2$O$_3$ polymorphs have been the catalytic support of choice for various profoundly important catalytic processes such as the selective catalytic reduction (SCR) of NO$_x$ species [1] and NO$_x$ storage [2]. H$_2$O adsorption on solid metal oxide surfaces is a key step in these catalytic systems in which the nature of the interaction between water and the metal oxide surface, as well as its interaction with other reactants, dictate the fundamental reactivity and selectivity trends.

Water adsorption on metals and metal oxide surfaces has thoroughly been discussed in the literature [3,4]. According to these reports, there is a strong interaction between the adsorbed water species and oxide surfaces. Commonly, at relatively low coverages, H$_2$O is found to adsorb molecularly on the cation sites of the oxide surface leading to isolated water molecules lacking intermolecular hydrogen bonding. The typical adsorption configuration of H$_2$O to the oxide surface under these conditions involves bonding between the Lewis acid sites of the oxide (i.e., cationic sites) and the lone pair of the O atom in the water molecule. As the coverage of adsorbed water is increased, formation of hydrogen bonds interlinking originally isolated H$_2$O molecules are observed which eventually results in crystalline or amorphous multilayer ice formation. The nature of H$_2$O adsorption (i.e., molecular or dissociative) on alumina surfaces seems to be closely related to the Al$_2$O$_3$ structure. Although H$_2$O was reported to adsorb molecularly on ordered $\gamma$-Al$_2$O$_3$/NiAl(110) thin films [5], it was found to adsorb dissociatively on Al$_2$O$_3$/Al(111) [6], $\alpha$-Al$_2$O$_3$(0001) [7], and $\gamma$-Al$_2$O$_3$/NiAl(100) [8].

In this presentation we will focus on the properties of ordered $\theta$-Al$_2$O$_3$ ultra thin films grown on a NiAl(100) single crystal substrate whose stoichiometry, morphology, and chemical structure can be analyzed in detail with conventional surface analysis probes. Therefore, the nature of the interaction between $\theta$-Al$_2$O$_3$ polymorphs with adsorbed H$_2$O can be thoroughly investigated, and related to the structural properties of the alumina thin films.

Materials and Methods

The structure of an ordered, ultra thin $\theta$-Al$_2$O$_3$ film grown on a NiAl(100) single crystal surface was studied by Auger electron spectroscopy (AES), X-Ray photoelectron spectroscopy (XPS), and low energy electron diffraction (LEED), and its interaction with water was investigated with temperature programmed desorption (TPD), and XPS.

Results and Discussion

Our results can be summarized as follows:

(a) H$_2$O adsorption on $\theta$-Al$_2$O$_3$/NiAl(100) surface is predominantly molecular rather than dissociative.

(b) For $\theta_{H2O} < 1$ ML, H$_2$O molecules populate Al$^{3+}$ cation sites (fig.1) to form isolated H$_2$O species ordered in rows along the cation sites of the oxide surface. Repulsive interactions between these adsorbed water molecules are indicated by a significant reduction in the desorption temperature with increasing H$_2$O coverages up to 1 ML.

(c) For $\theta_{H2O} > 1$ ML, H$_2$O overlayers were observed to form three dimensional ice multilayers. Water molecules occupy both cationic and anionic adsorption sites on the oxide surface allowing the formation of hydrogen bonding in the ice network.

(d) A small extent of H$_2$O dissociation was observed to occur on the $\theta$-Al$_2$O$_3$/NiAl(100) surface which was attributed to the presence of a low concentration of surface defects. Titration of the defect sites with adsorbed H$_2$O molecules revealed a defect density of ~0.05 ML for the $\theta$-Al$_2$O$_3$/NiAl(100) system consistent with the highly ordered nature of the oxide film suggested by the LEED images.

Figure 1. Schematic illustrating the $\theta$-Al$_2$O$_3$/NiAl(100) surface structure and the H$_2$O adsorption on the oxide film at $\theta_{H2O} \leq 1$ ML.

Significance

Well-controlled synthetic methods for preparing model catalysts whose chemical and catalytic properties can be fine tuned and investigated using atomic-level surface science probes will facilitate a deeper understanding of catalyst structure-function relationships sufficient for the design of highly active as well as selective technical catalysts which are crucial for many commercial processes such as selective catalytic reduction of NO$_x$.

References