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Ag Adsorption on Various Silica Thin Films

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Various defect sites on SiO₂ thin films on Mo(112) have been characterized with metastable impact electron spectroscopy (MIES), and the interaction between deposited Ag and these defect sites investigated with MIES/ultraviolet photoelectron spectroscopy (UPS). MIES/UPS data for low- and high-defect SiO₂ surfaces acquired as a function of Ag exposure are consistent with two-dimensional Ag growth at low coverage and three-dimensional growth at higher Ag coverages. With increasing defect density on the SiO₂ surfaces, no significant change is observed in the behavior of the work function with respect to the Ag coverage, suggesting that the interaction between Ag and SiO₂ is not influenced markedly by the presence of defects. This result is consistent with recent theoretical results that indicate a strong covalent bond between an overlayer metal and defect sites of SiO₂.

1. Introduction

The interaction of metals with oxides is central to various technologies such as heterogeneous catalysts, electronic devices, coatings, and chemical sensors. However, investigations with surface analytical methods involving charged particle probes have been limited because of surface charging problems arising from the insulating nature of many oxides. Such difficulties can be circumvented with the use of thin films of the oxide, films that have been shown to exhibit geometric, electronic, and chemical properties of the bulk counterpart, yet sufficiently conducting to avoid charging.^{1–3} A number of oxide systems have been studied using this methodology, including MgO, Al₂O₃, TiO₂, and SiO₂.^{1–6} Recently, single crystalline SiO₂ thin films (0.5–0.8 nm) have been prepared on Mo(112),^{4,5} and their electronic properties shown to be essentially identical to those of bulk SiO₂.⁶

Because metals generally interact weakly with oxide surfaces, three-dimensional metal growth typically occurs. Defect sites, however, can lead to a much stronger interaction between the oxide and the metal,^{7–10} leading to preferential nucleation of metal atoms at defect sites.^{11,12} Moreover, defect sites can modify the electronic and chemical properties of supported metals, especially as a result of charge transfer between the substrate and the

metal cluster.^{10,13,14} As a consequence, defect sites are thought to play a important role in altering the properties of oxide-supported metal catalysts.

In this work, low- and high-defect crystalline SiO₂ surfaces have been synthesized on Mo(112), and the various defect sites characterized with metastable impact electron spectroscopy (MIES). In addition, the interaction of Ag with these SiO₂ surfaces of varying defect concentration has been studied by MIES and ultraviolet photoelectron spectroscopy (UPS). Ag was chosen because of its relevance to a variety of catalytic processes. Recently, highly dispersed Ag clusters have been shown to exhibit interesting size dependent variation for selective catalytic oxidation.¹⁵ The changes in the MIES spectrum of SiO₂ as a function of Ag exposure is consistent with 2D growth at low Ag coverages, followed by 3D growth at higher coverages. With increasing defect density there is little change in the work function with varying Ag coverage, as has been seen for Ag on MgO, suggesting that the bonding between Ag and SiO₂ is primarily covalent and does not depend to a large extent on the defect concentration.

2. Experimental Section

The experiments were carried out in an ultrahigh vacuum (UHV) system (base pressure $\sim 1 \times 10^{-10}$ Torr) consisting of two interconnected chambers. One chamber is equipped with an ion gun for sputtering, low-energy electron diffraction (LEED), and temperature-programmed desorption (TPD). The second chamber is equipped with Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and MIES/UPS. MIES/UPS spectra were measured simultaneously with a cold-cathode discharge source^{16,17} that provides both ultraviolet photoelectron and metastable He 2³S ($E^* = 19.8$ eV) atoms with thermal kinetic energy. Metastable and photon contributions to the signal were separated by a time-of-flight method with a mechanical chopper. MIES and UPS spectra were acquired with incident photon/metastable beams at 45° with respect to the surface normal by use of a double-pass cylindrical mirror analyzer (CMA). The resolution of our analyzer, estimated by the width of the Fermi

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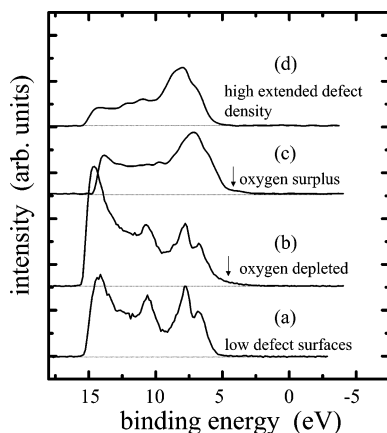


Figure 1. MIES spectra collected from four differently prepared SiO_2 surfaces: (a) a low-defect SiO_2 surface produced by a 1200 K anneal; (b) an oxygen-depleted surface prepared by Si deposition on SiO_2 ; (c) an oxygen-surplus surface prepared by oxygen treatment of Si/SiO_2 at 800 K; and (d) a surface prepared by annealing at 1050 K with a high density of extended defects.

edge, is approximately 0.4 eV. The energy denoted by E_F in the spectra corresponds to electrons emitted from the Fermi level of the Mo substrates. In the spectra reported herein, all the binding energies are referenced to E_F .

The Mo(112) sample was cleaned by repeated heating to 2200 K, and the sample cleanliness was confirmed by AES and LEED. Low-defect SiO_2 thin films on Mo(112) were prepared by deposition of Si at room temperature, followed by annealing at 800 K in O_2 at 1×10^{-7} Torr. The SiO_2 films were further annealed at 1200 K in O_2 at 1×10^{-7} Torr. The AES spectra of the SiO_2 thin films showed a Si^{4+} feature at 78 eV and no Si^0 feature at ~ 90 eV, indicating that Si is completely oxidized to SiO_2 .^{4,5} For a SiO_2 thin film with a thickness of 0.4–0.7 nm, determined by the attenuation of the AES Mo peaks, LEED showed a distinctive $c(2 \times 2)$ periodicity, indicating the formation of well-ordered SiO_2 networks.^{4,5} Prior to Ag deposition, the evaporation source [tungsten filaments wrapped with an ultrahigh pure (99.99%) Ag wire] was thoroughly outgassed. The break point in a plot of Auger intensity versus deposition time for Ag deposited on Mo(112), deemed to be one monolayer, ML, was used to calibrate the Ag evaporation source.

3. Results and Discussion

MIES spectra for the various SiO_2 surfaces are compared in Figure 1. A low-defect SiO_2 surface produced by a 1200 K anneal (Figure 1a) shows well-defined O(2P) features at 6–9 eV and features at 12 eV related to the Si–O bond. A second surface, prepared by annealing at 1050 K (Figure 1d), exhibits broader O(2P) features, indicative of an increased extended defect density; however, no band gap states are apparent, consistent with a low point defect density.⁶ It should be emphasized that MIES is an extremely surface-sensitive technique, which can identify defect sites far below 1%. For the oxygen-depleted surface prepared by Si deposition on SiO_2 (Figure 1b) and the oxygen-surplus surface prepared by oxygen treatment of a Si/SiO_2 surface at 800 K (Figure 1c), band gap states are apparent, consistent with the formation of oxygen vacancies or oxygen surplus sites.¹⁸ For more details of the SiO_2 film characterization, see ref 6.

MIES and UPS spectra collected from a low-defect SiO_2 surface as a function of Ag coverage at room temperature are shown in Figures 2 and 3. With increasing Ag coverage, the O(2P) feature attenuates, and concomitantly new Ag-related features appear. On the basis of previous results from Kempter and co-workers,¹⁹ the Ag-related features between 2 and 10 eV in MIES are attributed to

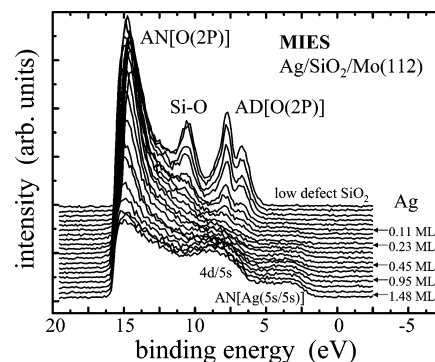


Figure 2. MIES spectra collected from a low-defect SiO_2 surface as a function of Ag exposure.

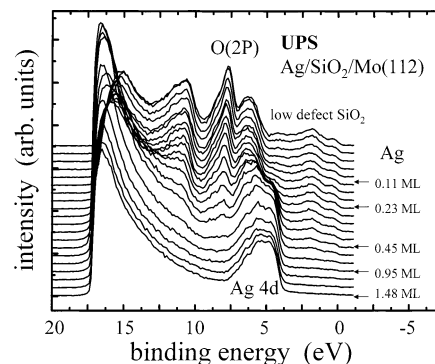


Figure 3. UPS spectra collected from a low-defect SiO_2 surface as a function of Ag exposure.

the electron emission from Ag 5s and 4d bands and arise from a combination of resonance ionization (RI) and Auger neutralization (AN) mechanisms. Due to the relatively high work function of Ag, no Auger deexcitation features for Ag are observed.²⁰ The feature at 14 eV corresponds to the (RI + AN) feature of SiO_2 –O(2P), i.e., He^+ formed at Ag clusters via the RI mechanism interact with the bare SiO_2 surface, and as a consequence, electrons are emitted from the O(2P) band of SiO_2 via the AN process. For a more detailed description of this MIES mechanism, see refs 19 and 20.

In Figure 4, the Ag(5s/5s)-AN and O(2P)-AN features as well as the work function versus the Ag coverage (from the data of Figures 2 and 3) are summarized. The work function data of Figure 4b were acquired by noting the energy of the onset of secondary electrons in UPS. The O(2P)-AN feature initially grows as a function of the Ag coverage because the number of He^+ produced by the RI mechanism at the Ag clusters increases with increasing Ag coverage.¹⁹ At higher Ag coverages, the intensity of the O(2P)-AN feature is reduced because the area of the uncovered SiO_2 surface decreases.¹⁹ The intensity of the Ag(5s/5s)-AN feature increases linearly initially, whereas at higher Ag coverages (above 0.5 monolayer) the growth rate of this feature is attenuated. The work function (Figure 4b) decreases rapidly at the initial stage of the Ag exposure and is followed by a slight increase at Ag coverages above 0.5 ML. The linear increase in the intensity of the Ag(5s/5s)-AN feature and the linear decrease of the work function at the early stage of Ag deposition may suggest that the Ag initially wets the SiO_2 surface, i.e., 2D clusters are formed. Above a coverage of

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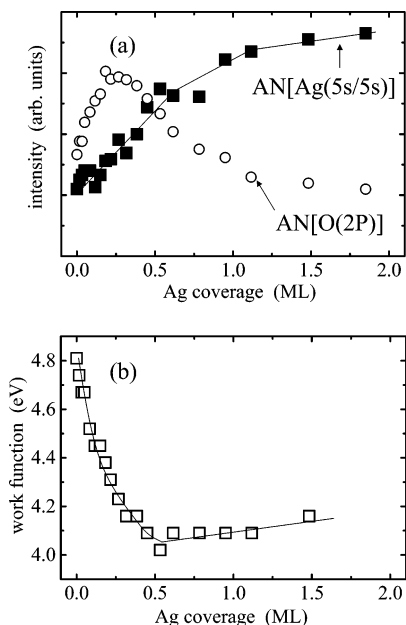


Figure 4. (a) Changes in the intensities of the MIES O(2P)-AN and Ag (5s/5s)-AN features, and (b) work function from a low-defect surface as a function of Ag coverage as determined by the onset of secondary electrons in UPS.

0.5 ML, Ag likely grows with a 3D morphology, leading to the attenuated change in the work function and intensity of the Ag (5s/5s)-AN feature. For Ag/MgO systems similar changes of the AN feature intensities also have been interpreted in terms of a 2D–3D transition.¹⁹ It is noteworthy that a 2D–3D transition in the growth mode of metal clusters with increasing metal coverage has been observed for several metal/oxide systems.^{21–23}

The work function of Ag is between 4.1 and 4.6 eV, depending on the surface morphology,²⁴ whereas the work function for SiO₂ films is approximately 5.0 eV. Considering that the work function of a nonuniform surface is simply the geometrical average of the local work functions and that the work function of the Ag clusters is constant as a function of Ag coverage, a monotonic decrease in the work function with increasing Ag exposure is anticipated. The data, however, show an initial decrease of the work function at relatively low Ag coverages, followed by an increase as the Ag coverage is increased above 0.5 ML (Figure 4b). The most plausible explanation for the minimum in the work function as a function of Ag coverage is that, at relatively low Ag coverages, Ag clusters become partially positively charged via transfer of electronic charge from Ag to SiO₂. Similar work function changes for Ni/TiO₂,²⁵ Ag/MgO,¹⁹ and Cu/ZnO²² have been interpreted in terms of charge transfer from the metal to the oxides. Previous XPS studies have also indicated that charge transfer from Ag to SiO₂ takes place,²⁶ consistent with the present data. Also, recent theoretical calculations for the Cu/SiO₂ system have shown that metal clusters can become charge-deficient on a perfect SiO₂ surface, leading to electrostatic bonding between the metal cluster

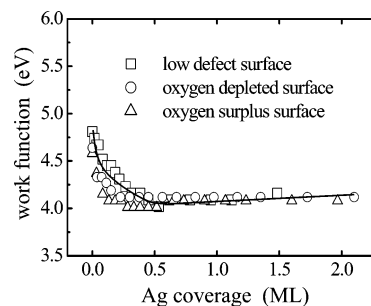


Figure 5. Work function changes for various SiO₂ surfaces as a function of Ag coverage determined by the onset of secondary electrons in UPS. The oxygen-depleted surface was prepared by Si deposition on SiO₂, and the oxygen-surplus surface was prepared by oxygen treatment of a Si/SiO₂ surface at 800 K.

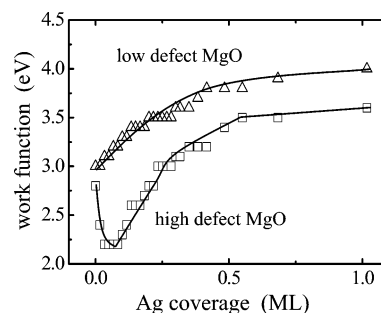


Figure 6. Work function changes from UPS for low- and high-defect MgO surfaces as a function of Ag coverage. The high-defect MgO surface was produced by sputtering and heating the low-defect MgO surface to 600 K.

and two nearest-neighbor O atoms. That is, polarization of charge on the metal cluster can occur in the absence of defects. An alternative but less likely explanation for the minimum in the work function as a function of Ag coverage is that the smaller clusters exhibit greater surface roughness, giving rise to significantly lower local work functions.²⁷

To obtain a better understanding of the interactions between Ag and defect sites on SiO₂, MIES/UPS data were acquired as a function of Ag exposure on SiO₂ surfaces with varying defect densities. Ag adsorption on various SiO₂ surfaces yields similar changes in MIES and UPS compared with the data of Figures 2 and 3, i.e., a decrease in the O(2P) feature, an increase in the Ag-related features, and an initial increase followed by a decrease in the intensity of the O(2P)-AN features, with increasing Ag exposure. The work function changes of the defective SiO₂ surface as a function of Ag exposure are quite analogous to those of the low-defect SiO₂ surface (Figure 5). These results are markedly different in comparison with the corresponding data for MgO(100),¹⁰ shown in Figure 6. For a high-defect MgO surface a pronounced minimum at low Ag coverage occurs, whereas for a low-defect MgO surface, the work function gradually increases with increasing Ag exposure. For various SiO₂ surfaces there is no significant influence of defect density on the work function as a function of the Ag coverage, i.e., the three curves in Figure 5 are almost identical. For the SiO₂ films the changes of the work function as a function of the Ag coverage for high- and low-defect surfaces are much less pronounced than for MgO, a more ionic oxide than SiO₂.

It is generally accepted that interactions of metals with defective oxide surfaces are much stronger than those with a defect-free oxide surface. According to recent

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theoretical studies,⁷⁻⁹ this is generally thought to be true for SiO₂. The work function data presented here indicate that the interactions of Ag with regular and defect sites are almost identical in terms of the electrostatic interaction resulting from the partial charge transfer from Ag to the substrate. These results suggest that, relative to regular sites, the interaction between Ag and defect sites on SiO₂ may be enhanced by relatively strong covalent bonds. Recent theoretical investigations have shown that transition metals such as Pd and Cu and various point defects on SiO₂ form strong covalent bonds,^{8,9} whereas for MgO, enhanced charge transfer between point defects and adsorbed metals has been suggested.^{13,14,28} The results found in these recent theoretical studies are consistent with the work function data for SiO₂ and MgO presented here (Figures 5 and 6).

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4. Conclusions

The adsorptive behavior of Ag on low- and high-defect SiO₂ surfaces has been studied with MIES and UPS. Changes of the MIES spectrum of a low-defect SiO₂ surface as a function of Ag exposure can be interpreted in terms of 2D growth at low Ag coverages, followed by 3D growth at higher coverages. In contrast to previous studies on MgO, charge transfer between Ag and SiO₂ is not significantly enhanced in the presence of defect sites, suggesting that the bonding between Ag and defect sites on SiO₂ is primarily covalent.

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