The encapsulation of Fe on $TiO_2(110)$

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We report evidence in this letter for the encapsulation of Fe clusters supported by single crystal TiO_2. After thermal annealing in ultrahigh vacuum (UHV) at 500–700°C for several hours, Fe clusters are almost completely covered by Ti suboxides TiO_x while Fe remains mainly in the metallic state. The phenomenon can be clearly measured using LEIS (low energy ion scattering) and XPS (X-ray photoelectron spectroscopy).

Keywords: Iron; titanium dioxide; ultrathin films; SMSI

1. Introduction

The so-called strong metal–support interaction (SMSI) has been widely studied on metal/TiO_2 systems [1,2]. In early studies it was reported that interactions between metal particles and TiO_2 result in suppression of H_2 and CO chemisorption [3]. From the results of various experiments, it was suggested that the physical cause of this suppression is the migration of a suboxide of the support onto the metal particles induced by high temperature reduction in H_2 [1,3–7].

This letter reports evidence for a complete encapsulation of Fe clusters supported on a single crystal $TiO_2(110)$ surface caused by ultrahigh vacuum (UHV) thermal annealing up to 500–700°C. The encapsulated Fe clusters remain metallic. It is worth noting that UHV is sufficient to partially reduce the support TiO_2 in the absence of H_2 ambient [6]. The combination of X-ray photoelectron spectroscopy (XPS) and low energy ion scattering (LEIS) enables us to observe the segregation of TiO_x onto Fe clusters.

2. Experimental

The experiments are performed in a UHV system including an X-ray source for

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XPS and a differentially pumped ion gun for LEIS. A 100 mm radius concentric hemispherical analyzer is used for XPS in the fixed analyzer transmission (FAT) mode and for LEIS in the fixed retarding ratio (FRR) mode. The chamber base pressure is $\leqslant 2 \times 10^{-10}$ Torr, and it is maintained at $3\text{–}4 \times 10^{-10}$ Torr during deposition from a shielded, liquid N_2-cooled metal evaporation source. The typical Fe equivalent thickness is 10 Å for the thermal annealing experiments described here. The thickness is determined using a Quartz Crystal Monitor [8].

The support oxide is a polished single crystal of TiO_2 with (110) surface orientation. The TiO_2 crystal has been annealed to 1000–1100 K in UHV for hours so that the bulk is reduced sufficiently to become conductive. Then the crystal is annealed in 2×10^{-6} Torr of O_2, so that a stoichiometric TiO_2 surface is restored (as characterized by XPS and LEED). The thermal annealing is performed by electron bombardment from a filament placed at the back of the crystal [9].

LEIS is an extremely surface sensitive technique. Due to the very high ion neutralization probability, only the probe ions scattered from the topmost surface atoms can survive and be detected [10,11]. $^{20}Ne^+$ ions with 1.5 keV primary energy are used for both LEIS measurements and surface sputtering depth profiles. LEIS is performed at an incident angle of 40° from the surface normal and a fixed scattered angle of 135°, where no obvious shadowing effect is observed.

XPS is used to monitor the valence state of deposited Fe and the reduction of the support oxide TiO_2, following Fe deposition and thermal annealing. Reduced Ti states, Ti^{3+} and Ti^{2+}, are observed and can be separated from Ti^{4+} due to different binding energies of Ti 2p emission. Most XPS spectra are measured with the sample surface normal 10° off the analyzer axis (to avoid the strong XPS forward focusing effect [12]), unless otherwise specified. Using LEIS combined with XPS, we observe evidence for complete encapsulation of the Fe by suboxide TiO_x following annealing in the range 500–700°.

3. Results

As shown in fig. 1, the clean $TiO_2(110)$ surface yields sharp Ti 2p peaks corresponding to photoemission from the Ti^{4+} state alone (fig. 1A(a)). Following room temperature Fe deposition, the Ti 2p spectrum has lower intensity and a broader line shape as well, fig. 1A(b). In addition to attenuation of Ti^{4+} photoemission by overlayer Fe, the Ti cations in the support oxide are reduced to a lower oxidation state (Ti^{3+}) due to the interfacial chemical interaction, i.e. the oxidation of deposited Fe and the reduction of Ti at the interface. From the Fe 2p XPS spectra (fig. 1B(a), top curve), we observe that the dominant species is metallic Fe at average Fe thicknesses about 10 Å. Only at the very interface, there are FeO_x species that we identify with the interfacial interaction [8,6].

Fig. 2(a) is an LEIS spectrum of the $TiO_2(110)$ surface covered with 10 Å of Fe as deposited at room temperature. The support oxide TiO_2 is almost completely

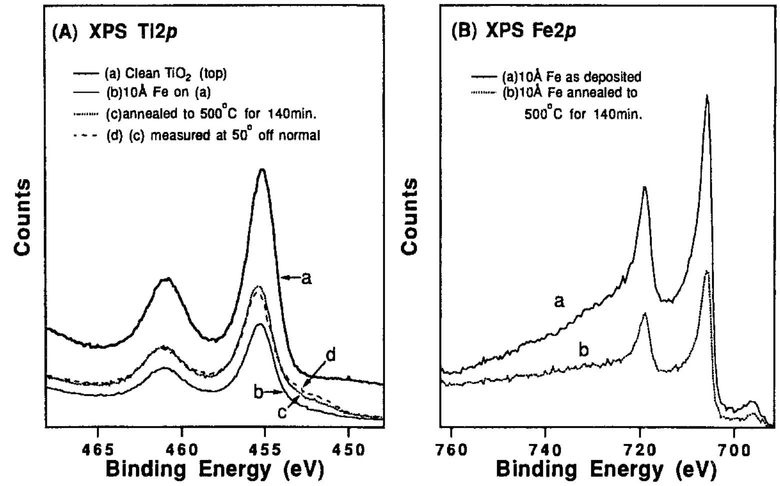

Fig. 1. (A) XPS Ti 2p spectra of (a), clean stoichiometric $TiO_2(110)$ (thick solid curve), (b) $TiO_2(110)$ with 10 Å of Fe as deposited (thin solid curve at bottom), (c) surface (b) after annealing to 500°C for 140 min measured at 10° off surface normal (dotted line), and (d), surface (b) after annealing to 500°C for 140 min measured at 50° off surface normal (dashed line). (B) XPS Fe 2p spectra of (a), 10 Å of Fe on $TiO_2(110)$ surface as deposited (solid line), and (b), 10 Å of Fe on TiO_2 after annealing to 500°C for 140 min (dotted line).

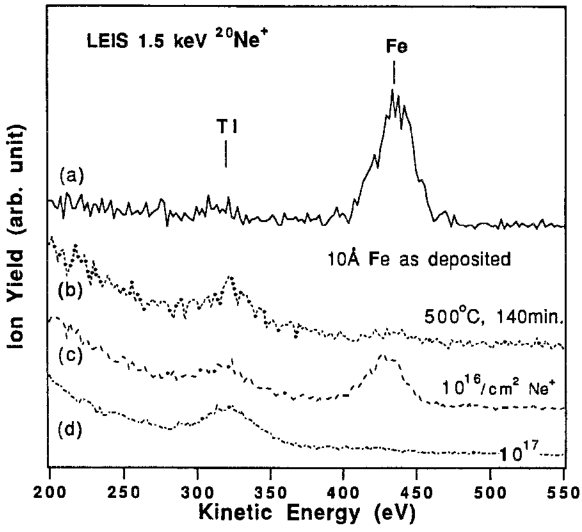

Fig. 2. LEIS spectra using 1.5 keV $^{20}Ne^+$ ions. (a) 10 Å of Fe on $TiO_2(110)$ surface as deposited, (b) after annealing surface (a) to 500°C for 140 min, (c) after sputtering surface (b) by 1.5 keV Ne^+ with total dose ~ $10^{16}/cm^2$, (d) after sputtering surface (b) by 1.5 keV Ne^+ with total dose ~ $10^{17}/cm^2$.

covered by overlayer Fe so that the dominant peak in the spectrum is due to the ions scattered from Fe atoms. This is consistent with the substantial decrease of Ti 2p intensity in XPS.

The thermal annealing is performed in UHV. At 500°C, after 140 min annealing, the Ti intensity increases and Fe intensity decreases shown in the XPS spectra of fig. 1A(c) and fig. 1B(b). Some observations can be made from fig. 1: (1) After 140 min annealing at 500°C, the Fe 2p intensity is lower, and the Fe $2p_{3/2}$ peak (fig. 1B(b)) is narrower than in the as-deposited case (fig. 1B(a)), in the direction of metallic Fe. (2) Comparing curves (a) and (b) in fig. 1B, the ratio of the peak height to the background at kinetic energies around 30 eV lower than the Fe 2p peak energy (higher binding energy) is different. Curve (b) in fig. 1B has higher relative background than curve (a), indicating more inelastic processes. As discussed in ref. [13], such pronounced inelastic loss features are consistent with the presence of Fe in the subsurface region. (3) The Ti 2p spectrum (dotted line fig. 1A(c) in left panel) shows an increase in the lower binding energy shoulder (the shoulder is broader than that in fig. 1A(b)). The lower binding energy shoulder is due to photoemission from Ti cations with lower oxidation states, i.e., Ti^{3+} (1.8 eV lower binding energy than Ti^{4+} $2p_{3/2}$) and Ti^{2+} ($\sim$ 3.6 eV lower than Ti^{4+}) [14–16]. (4) Compared to the Ti 2p spectrum before annealing (curve (b) in fig. 1A), where only Ti^{4+} and Ti^{3+} are observed, the spectrum obtained after annealing at 500°C shows a greater increase of the Ti^{2+} state (curves (c,d)). This is consistent with previous reports of the formation of a suboxide TiO_x with $x \approx 1$ [1]. All of the XPS measurements discussed above are at 10° off the surface normal. The emission from these reduced states is even more pronounced if the measurement is made at 50° off the surface normal (dashed line fig. 1A(d) in left panel). This indicates that the reduced Ti cations are located in the surface region because of the higher surface sensitivity of the more glancing angle measurements.

Meanwhile, the LEIS spectrum of fig. 2(b) shows that after annealing at 500°C for 140 min, the Ti peak becomes dominant and the Fe peak is greatly attenuated.

The combination of LEIS and XPS results indicates that a possible process during thermal annealing could be the migration of Ti suboxides onto Fe, or so-called "encapsulation", while Fe might form metallic clusters rather than a continuous film because it is energetically favorable. This is consistent with the XPS measurements which show that Fe is more metallic after annealing and the Fe photoemission intensity is lower.

To test the encapsulation model, sputtering depth profiles have been measured after high temperature ($\geqslant$500°C) thermal annealing. 1.5 keV Ne^+ is used for both LEIS measurements and sputtering. Fig. 2(c) shows that after sputtering with 1.5 keV Ne^+ (total dose about $1 \times 10^{16}/cm^2$), the Fe peak reappears and becomes rather pronounced. This is consistent with the exposure of encapsulated Fe clusters at the surface after the top Ti suboxide layer is sputtered off. Further sputtering, up to a total Ne^+ dose about $6 \times 10^{16}/cm^2$, causes sputtering and removal of the Fe clusters. Fig. 2(d) is the Ne^+ LEIS spectrum of a surface after about $10^{17}/cm^2$ of

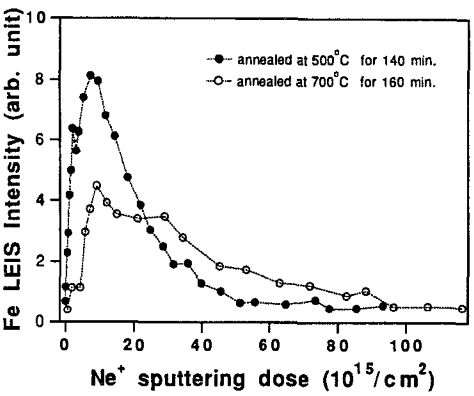

Fig. 3. LEIS Fe intensities for 10 Å of Fe supported on $TiO_2(110)$ surface after annealing in UHV at 500°C for 140 min (solid dots), or annealing at 700°C for 160 min (open circles) as functions of Ne^+ sputtering dosage. $^{20}Ne^+$ ions with 1.5 keV primary energy are used for both sputtering and LEIS measurements.

Ne^+ sputtering; only support Ti oxide is observed and Fe has been sputtered away.

A sputtering depth profile for 10 Å of Fe after 140 min of annealing at 500°C is plotted in fig. 3 (solid circles). The LEIS Fe intensity is plotted as a function of Ne^+ sputtering dosage. It is clear that the Fe clusters are in the subsurface region. For comparison, a depth profile of 10 Å Fe on TiO_2 after 160 min annealing at 700°C is also plotted in fig. 3 (open circles). It appears that the Fe clusters are located deeper in the supporting oxide as a result of higher temperature annealing. Consistently, the total areas under the depth profiles are approximately the same for both 500 and 700°C annealing, which indicates no loss of Fe due to evaporation or bulk diffusion at these temperatures.

4. Summary

We report evidence in this letter for the encapsulation of Fe clusters supported by single crystal TiO_2 after thermal annealing in ultrahigh vacuum (UHV) at 500–700°C. In less than three hours, UHV annealing causes Fe clusters to be almost completely covered by Ti suboxides TiO_x, while Fe remains mainly in the metallic state. The phenomenon can be clearly measured using LEIS and XPS.

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