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First STM Observation of Silica and Platinum-on-Silica Model Catalyst Systems

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Scanning tunneling microscopy (STM) images of silicon oxide surface and of Pt ultrafine particles deposited on it were obtained for the first time. The silicon oxide sample employed consists of a thin (ca. 0.7 nm thick) native silica film present on a Si(100) surface. The STM observation of these sample systems was critically dependent on the choice of the electron tunneling conditions.

Scanning tunneling microscopy (STM) is a powerful tool for the studies of solid surfaces, because of high spatial resolution and spectroscopic capabilities inherent to it.[1] Its application, however, has been largely limited to electroconductive materials, due to its operating principles which depends on the tunneling current that flows between the probe tip and the sample surface. For the study of non-conductive material surfaces, atomic force microscope (AFM) has been developed,[2] which relies on the atomic forces exerted in between the atoms on the probe tip and those on the sample surface and thus does not require electrical conductivity on the sample. A drawback of AFM, however, is that it provides only the topographic images of sample surfaces and no spectroscopic information.

In this context, it would be of great practical interest to establish a procedure which enables the STM study of non-conductive material surfaces. Works aimed toward this end is scarce.[3] In the present paper we describe a procedure which employs the use of thin film of a non-conductive material, thus compensating its low conductivity, and then optimizing the tunneling conditions for its STM observations.

Silica and Pt-deposited-on-silica were chosen as model samples. This particular choice of the sample systems reflects our interest in the STM study of industrial supported metal catalysts.[4-6] Thin film of silicon oxide present on a commercial B-doped silicon (100) surface was employed as a silica sample. Its thickness was estimated from the Si 2p X-ray photoemission peak intensities to be ca. 0.7 nm. Platinum was vacuum-deposited on the surface of this silica film. The amount of Pt deposited was also determined by XPS. A home-built STM equipment which exhibit atomic resolution for graphite crystals and resolves monoatomic steps of metal surfaces was operated under ambient conditions for the observations of these sample surfaces.

The STM observations of these sample surfaces were found to be critically dependent on the tunneling conditions, particularly the tunneling voltage V_t. It is common to employ V_t of ca. 1 V for the STM observations of semiconducting silicon surface, because this places V_t above its band gap and in its conduction band. Similarly, one should be able to tunnel electrons into the conduction band of "non-conducting" materials if one employs V_t above its band gap. For the thin film of silicon oxide formed

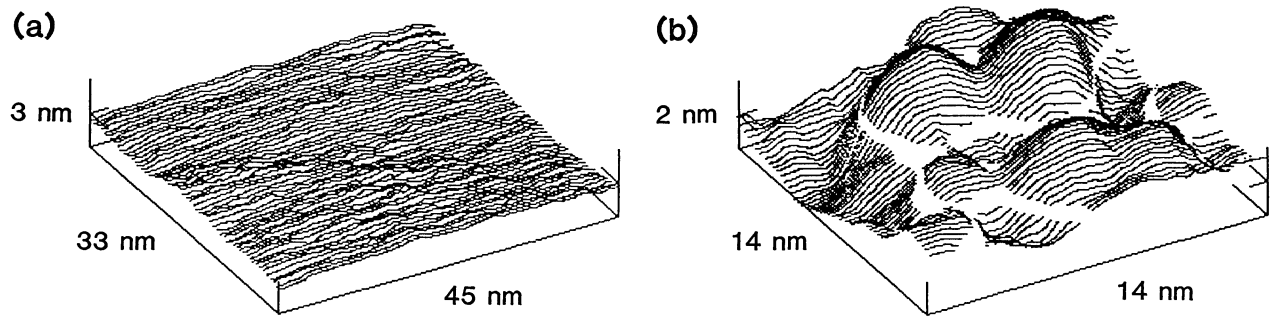

Fig. 1. STM images of (a) the native oxide surface present on a Si(100) surface and (b) Pt particles vacuum-deposited on the surface of this thin silica film. V_t=4.0 V, I_t=0.1 nA, tip negative.

on the surface of polycrystalline silicon its conduction band is placed ca. 3 eV above the lower edge of silicon conduction band,[7] and thus V_t of 4.0 V was chosen for the present STM observations. At this bias voltage electrons are expect to tunnel into the silica conduction band, thus imaging the silica surface and any conducting material placed on it. In fact, preliminary tunneling spectroscopic measurements indicate that when bias voltage is lowered from 4 V to 3 V ($\pm$ 0.5 V depending on the lateral position of the tip), tunneling current decreased sharply, and with constant current mode sudden tip movement toward the surface is observed. This apparently indicates the change in the tunneling channel at that voltage, supporting our contention that at 4 V the electrons are tunneling into the conduction band of the silica thin film. Details of these spectroscopic measurments and voltage-dependent STM images will be published elsewhere.[8]

Figure 1 shows representative STM images of these sample surfaces thus obtained. As may be apparent in Fig.1(a) the present silicon oxide surface is relatively flat, showing the terraces surrounded by steps of few angstroms heigh. When Pt is vacuum-deposited on this surface (Pt/Si atomic ratio=0.4), it is found from Fig.1(b) that Pt forms hemispherical particles of ca. 2 to 5 nm in diameter and 1 to 2 nm in height. This Pt-on-silica is a model system for the industrial Pt/SiO_2 supported metal catalysts as stated above, and we would like to stress that this is the first successful STM observation of such system. It is also noted that the Pt particles of this Pt/SiO_2 model catalyst system have appearances similar to those in Pt/C model catalyst system examined earlier.[5]

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