Surface-enhanced Infrared Spectrum of CO Adsorbed on Cu Electrodes in Solution

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A chemical deposition technique was employed for the first time in preparing thin Cu films showing extremely strong surface-enhanced infrared absorption effect for the molecules adsorbed on the surface. The enhancement was examined in an electrochemical environment by using CO as a model adsorbate. The result is compared with literature data by focusing on the band shape of the enhanced absorption.

Infrared (IR) absorption of molecules is enhanced significantly on thin metal films consisting of nanoparticles (islands).[1] The nanosized structure of the film facilitates the interactions of IR photons with the metal and adsorbed molecules, resulting in the enhanced absorption.[1] The so-called surface-enhanced infrared absorption (SEIRA) effect has been studied on many metal surfaces, mostly on Au and Ag island films prepared by vacuum evaporation. Compared with Au and Ag, SEIRA studies on Cu are very limited.[2–5] One of the reasons of this may be that Cu surface is oxidized easily. Since SEIRA is a relatively short-range effect decaying sharply within a few monolayer distance from the surface,[1] the enhancement effect could be reduced remarkably by the oxidation of the surface. In fact, the magnitude of the enhancement observed on Cu was less than that observed on Au and Ag.[3]

This problem can be avoided by preparing the sample and measuring the spectrum in an ultrahigh vacuum (UHV) system without exposing the sample to air. Despite the use of an UHV system, the enhancement factor[6] reported by Seki et al.[5] was only 5 for the CO stretching mode, ν(CO), of CO adsorbed on Cu island films prepared by electron-beam evaporation, while much larger enhancement factors of 20–40 and 15–75 have been reported on Au and Pt thin films, respectively.[7,8] In addition, the enhanced absorption band observed on the vacuum-evaporated Cu films was severely distorted to yield an asymmetric derivative-like shape,[5] which prevents the definition of the vibrational frequencies and quantitative analysis of the data. In this letter, we report that Cu films prepared by a chemical deposition technique exhibit a large enhancement comparable to other metals with normal (that is, symmetric) spectral shapes.

The SEIRA-activity of the chemically deposited Cu film was examined in an electrochemical environment, an alternate way to avoid the surface oxidation problem, by using CO as a model adsorbate. The measurements were performed with the Kretschmann ATR configuration (a prism/Cu film (electrode)/solution geometry). Experimental details were described elsewhere.[9] A Cu film (about 100 nm in thickness) was deposited on the total reflecting plane of a Ge hemicylindrical prism by contacting the Ge surface with a plating solution (0.04 M $CuSO_4 \cdot 5H_2O$ + 0.2 M EDTA·2Na + 0.2 M glyoxlic acid + 1 mM 2,2′-bipyridine adjusted at pH 13 with NaOH, where M = mole dm^{-3}) at 70 °C for 90 s. The deposited Cu film was electropolished in a H_3PO_4 solution (50 mL of 85% H_3PO_4 + 50 mL H_2O) at 1 A for 1 s before use to remove oxide layer.[10] After washing with ultrapure water, the electrode was transferred to an electrochemical cell by covering the surface with ultrapure water to prevent surface contamination. Finally, the surface was oxidized slightly and then reduced electrochemically in the test solution (0.1 M $KClO_4$) to clean the surface further. Electrode potentials were measured and quoted against an Ag/AgCl reference electrode. All spectra are shown in the absorbance units defined as $-\log(I/I_0)$, where I and I_0 represent single-beam spectra with and without CO in the solution, respectively.

AFM observation (Figure 1) reveals that thus prepared Cu films consist of well-separated metal particles with an average diameter of 150 nm. Depth profile analysis suggested that the height of the particles is around 50 nm, which is smaller than the average thickness of the film (100 nm). Therefore, the elliptic particles with an aspect ratio of about 3 are likely to exist on a 50-nm thick continuous film. In fact, the conductivity of the film was good enough for electrochemical measurements. The morphology of the Cu film is largely different from that of vacuum-evaporated Cu films: The Cu films that show pronounced band shape distortion are nearly continuous ones having many crevices.[5]

The solid trace in Figure 2 is a typical cyclic voltammogram of the electrode in Ar-saturated 0.1 M $KClO_4$. The cathodic current at potentials more negative than −0.9 V is due to hydrogen evolution. A corresponding data in the CO-saturated electrolyte is shown by the dotted curve. The suppression of hydrogen evolution suggests the adsorption of CO on the surface. The adsorption of CO is confirmed from Figure 3, in which a series of IR spectra of the electrode surface recorded simultaneously with the voltammogram are shown. A peak assigned to ν(CO) of CO adsorbed at atop site is seen at about 2080 cm^{-1}. The band is more intense at more negative potentials probably because of the competitive adsorption between CO and ClO_4^-.[11,12] Fur-

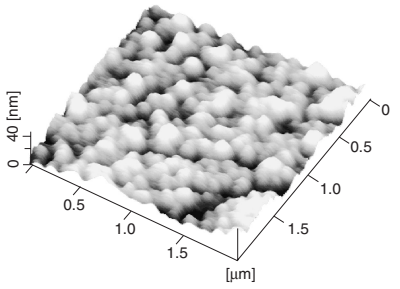

Figure 1. A typical AFM image of a chemically deposited Cu film on Ge.

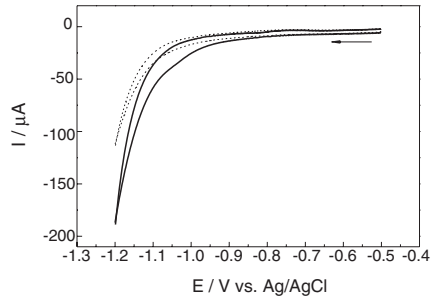

Figure 2. Cyclic voltammograms for the chemically deposited Cu film in Ar-saturated (solid trace) and CO-saturated (dashed trace) 0.1 M $KClO_4$. Sweep rate was 2 $mV \cdot s^{-1}$.

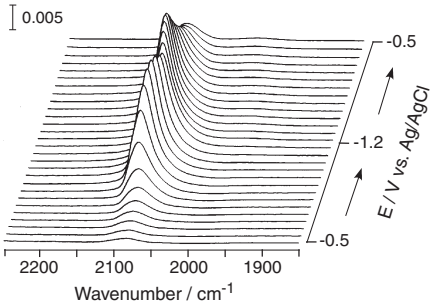

Figure 3. Series of IR spectra of CO adsorbed on the Cu electrode acquired simultaneously with the cyclic voltammogram in Figure 2.

ther detailed analysis of the competitive adsorption will be reported separately.

The peak intensity of the ν(CO) band at -1.0 V, for example, is 0.025, which is 12–25 times as intense as that observed on poly- and single-crystal Cu electrodes by IR reflection–absorption spectroscopy (IRRAS) (0.001–0.002).[11,12] The enhancement factor is nearly identical to that observed on Au[7] and Pt[8] island films, and much larger than observed on vacuum-evaporated Cu films.[5] It is obvious that a larger surface area of the island film (that is, a larger number of CO molecules adsorbed) contributes to the enhancement. However, the roughness factor of the electrode estimated from the double-layer charging current was only about 3, which is close to those for other chemically deposited metal films (2.5 for Au[7] and 7 for Pt[8]).

Besides the larger enhancement, it should be noted that the shape of the band observed on the chemically deposited Cu film is nearly symmetric as is observed on bulk electrodes by IRAS.[11,12] This is a marked difference from vacuum-evaporated Cu films, on which adsorbed CO shows an asymmetric derivative-like band.[5] Two theoretical models can explain the derivative-like band shape, as well as the IR-absorption enhancement. Krauth et al.[13] could simulated the distorted band shape of CO adsorbed on vacuum-evaporated Fe by assuming a coupling of the adsorbate vibration and electronic transitions of the metal induced by incident field (electron–hole pair excitation or collective electron resonance[5]). On the other hand, Bjerke et al.[14] simulated the band shape by using Fresnel equations and Bergman effective-medium approximation, which is based on a theoretical model by Osawa et al.[1] The electronic coupling Krauth et al. assumed is not included in the latter simulation and the asymmetric shape comes from the dispersion of the refractive index of the adsorbate around the vibrational frequency. The authors suggested that the distorted band shapes appear when nanoparticles are contacting or emerged with each other.

The model by Krauth et al. predicts that SEIRA is inevitably accompanied by the band-shape distortion. In contrast, the present experimental result clearly demonstrates that the spectral distortion of adsorbate vibration is not intrinsic nature of SEIRA, and that both band-shape and enhancement factor are controllable by tuning the morphology of the film, as has been suggested by Osawa et al.[1] and Bjerke et al.[14]

In summary, Cu thin films prepared by the chemical deposition technique exhibit larger SEIRA effect than vacuum-deposited Cu films. The enhancement factor for the former films was comparable to those of Au and Pt films. In addition, differently from vacuum evaporated Cu films, the band shape of CO adsorbed on the chemically deposited Cu film was nearly symmetric as observed on bulk Cu surfaces. The different SEIRA-activities of the Cu films prepared by the two techniques are ascribed to the difference in morphology.

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