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Surface-enhanced Raman scattering of the pyridine KCl-water-copper system: Temperature dependence

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Irreversible loss of surface-enhanced Raman scattering (SERS) intensity associated with adatomic instability, observable at room temperature in the silver-electrode SERS system, was found to be observable in the copper-electrode SERS system when the solution temperature was raised above 40 °C. Surface reflectance of the SERS electrode was found to increase during the irreversible loss of SERS intensity and thus depends on the adatom surface concentration and structure.

INTRODUCTION

Many experimental and theoretical studies of surface-enhanced Raman scattering (SERS) have shown that there are two important mechanisms of electrodynamic resonance effects and chemical effects operating in common to enhance Raman scattering from surface adsorbed molecules.[1-4] Electrodynamic resonance of surface-plasmon excitation was proved to be important in SERS from the experimental studies employing the attenuated-total-reflection (ATR) configurations, where they observed maximum SERS intensity at the minimum surface reflectance.[5,6] The excitation of the surface-plasmon polariton by the incident light would certainly bring about reduction of surface reflectance and enhancement of surface electric field. The surface reflectance of the SERS-active metal surfaces has been thus assumed to reflect the degree of excitation of the surface-plasmon polaritons.[5,6] On the other hand, irreversible loss of SERS intensity was observed when the solution or substrate temperature was raised above a certain temperature[7,8] and the electrode potential was decreased below a certain negative value.[9,10] These observations of irreversible loss of SERS intensities are considered to support either the adatomic charge-transfer effects in SERS (Ref. 2) or the localized-surface-plasmon effects[11,12] associated with extremely small pores or cavities[13,14] as a possible SERS mechanism. However, this irreversible loss of SERS intensity was not observed in the copper-electrode and copper-overlayered-silver-electrode systems[15] at room temperature in contrast with the silver-electrode system.

In the present work, we have first succeeded in observing the irreversible loss of SERS intensity from the copper-electrode SERS system at temperatures above 40 °C and also experimental evidence of adatomic effects on the surface reflectance of the SERS-active electrode surfaces.

EXPERIMENT

Deionized water and analytic grade chemicals were used to make the SERS systems of (0.05M pyridine)/(0.1M KCl)/water/Cu and (0.05M pyridine/(0.1M KCl)/water/Ag. Electrodes were prepared from the polycrystalline plates by surface polishing with alumina powders (0.3 and 0.05 μm) and surface etching in a NH_4OH/H_2O_2 solution for Ag and in a NH_3OH/H_2O solution for Cu. Nichrome wire enclosed in the glass tubing was used to heat and control the solution temperature. Potential measurements were made with respect to the saturated-calomel reference electrode (SCE). Laser lines of 5309 and 6471 Å from Ar-Kr mixed-gas laser were used through the echelon-grating tunable filter and a cylindrical lens for excitation of SERS. The SERS spectra were measured by use of the double-grating spectrometer (SPEX-1403) and the surface reflectance by use of a separate photodetector unit.

RESULTS AND DISCUSSION

Figure 1 shows the SERS spectrum of (0.05M pyridine)/(0.1M KCl)/water/Cu system at room temperature (21 °C). The SERS spectrum is seen to be well observable down to the electrode potential as low as $V = 1.8$ V_{SCE} and the potential dependence of the SERS line intensities was found to remain reversible in the non-Faradaic region of potential. However, when the solution temperature was raised to 45.5 °C as shown in Fig. 2, SERS lines were observed to vanish completely as the electrode potential was lowered to below $V = -1.5$ V_{SCE}. Furthermore, when the electrode potential was changed back to higher (less negative) potentials the SERS line intensities were not recovered in full but in small fraction around 10%. This irreversible loss of SERS intensities at the potential below the potential of zero charge (PZC) is attributed to the adatomic diffusion into surface defects.[9,10] We can thus see that Cu adatoms may be susceptible to the surface diffusion at $T = 45.5$ °C but not at $T = 21$ °C.

As shown in Fig. 3, we have made a simultaneous observation of both the SERS intensity at 1012 cm^{-1} corresponding to pyridine ring-breathing mode and the surface reflectance of the electrode during the electrode-potential scanning at the rate of 5 mV/sec. From Fig. 3 we can see that at $T = 23$ °C, the SERS intensity obtains maximum at $V_{max} = -0.9$ V_{SCE} and also reversible with respect to the change of potential in the range between $V = 0.0$ V_{SCE}

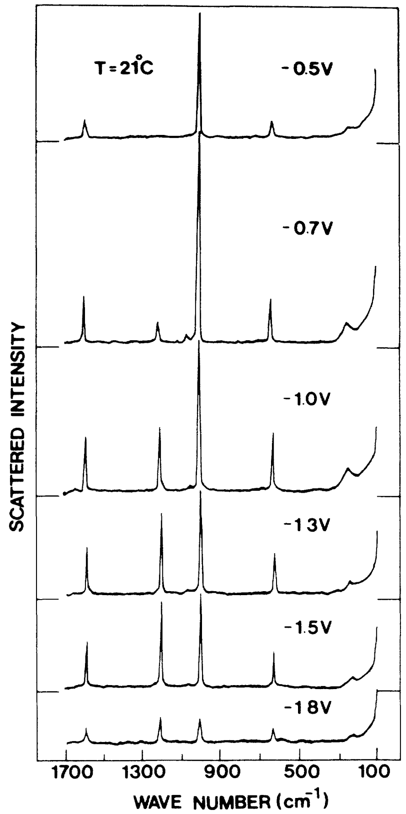

FIG. 1. Potential dependence of SERS spectra from (0.05*M* pyridine)/(0.1*M* KCl)/water/Cu electrode system at $T=21\,^{\circ}\mathrm{C}$. Laser excitation at 6471 Å.

and $-1.5\ \mathrm{V_{SCE}}$. The surface reflectance shows a minimum dip at a potential $V_{\min}\simeq-0.2\ \mathrm{V_{SCE}}$, corresponding to completion of oxidation, much higher (less negative) than $V_{\max}$ of the maximum SERS intensity and no change as from below $V=-0.55\ \mathrm{V_{SCE}}$. On the other hand, at $T=45.5\,^{\circ}\mathrm{C}$ SERS intensity drops sharply at $V=-1.45\ \mathrm{V_{SCE}}$, where a definite increasing change is observed in the surface reflectance. This loss of SERS intensity at $V=-1.45\ \mathrm{V_{SCE}}$ and $T=45.5\,^{\circ}\mathrm{C}$ is irreversible, that is, the SERS intensity is not recoverable by resuming the reverse cycle of potential back to higher (less negative) potentials. Since the large-scale roughness remains unchanged in the non-Faradaic region of the electrode potential, and the condition for surface-plasmon excitation is reversible with respect to the electrode potential change in this non-Faradaic region, the irreversible loss of SERS intensity observed at $V=-1.45\ \mathrm{V_{SCE}}$ cannot be ascribed to the surface plasmon effect. Furthermore, this observation of irreversible loss is possible only above $T=40\,^{\circ}\mathrm{C}$ and thus seems to be associated with the Cu-adatom diffusion. Adatoms are very much effective for electron-hole pair excitations[16,17] due to their localized densities of states and relaxations of symmetry selection rules. More adatoms at the surface thus mean a reduced surface reflectance due to adatomic absorption of incident light but increasing SERS due to enhanced charge-transfer excitations. Figure 4 shows that even at the solution temperature of $T=45.5\,^{\circ}\mathrm{C}$ the irreversible loss of SERS intensity is not

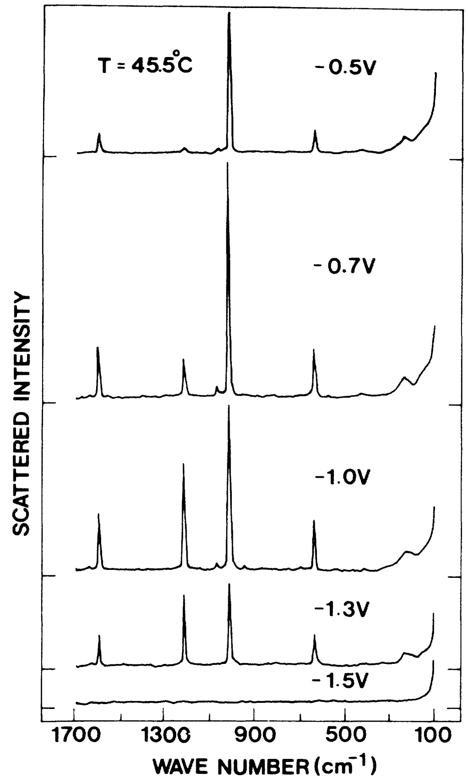

FIG. 2. Potential dependence of SERS spectra from (0.05*M* pyridine)/(0.1*M* KCl)/water/Cu electrode system at $T=45.5\,^{\circ}\mathrm{C}$. Laser excitation at 6471 Å.

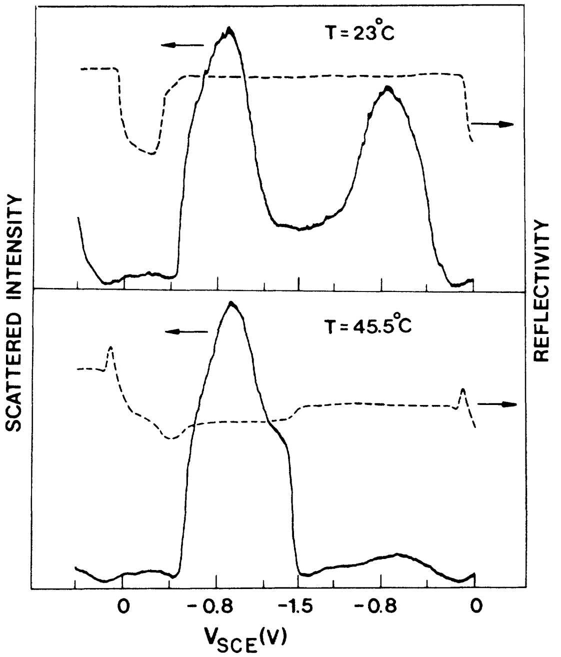

FIG. 3. Continuous trace of the pyridine SERS line intensity at 1012 $\mathrm{cm^{-1}}$ (solid line) and surface reflectance of the electrode during triangular ramps of the electrode potential in (0.05*M* pyridine)/(0.1*M* KCl)/water/Cu electrode system. Ramp rate at 5 $\mathrm{mV_{SCE}}$/sec in the range of potential $\mathrm{V_{SCE}}=0$ to $\mathrm{V}=-1.5\ \mathrm{V_{SCE}}$ and back to $\mathrm{V_{SCE}}=0$, with incident laser at 6471 Å.

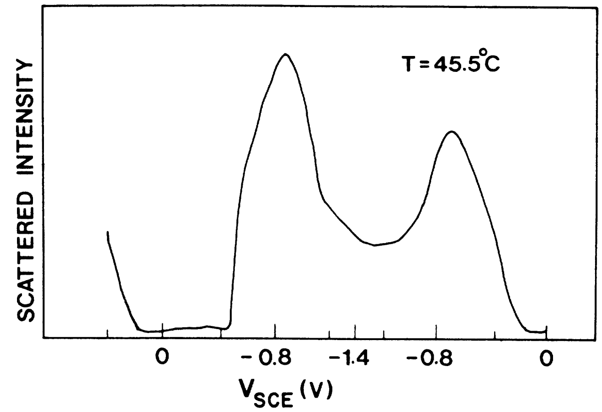

FIG. 4. Continuous trace of pyridine SERS line intensity at 1012 cm^{-1} during triangular ramps of the electrode potential in (0.05*M* pyridine)/(0.1*M* KCl)/water/Cu electrode system. Ramp rate at 5 mV_{SCE}/sec in the range of potential: $V_{SCE}=0$ to $V=-1.4$ V_{SCE} and back to $V_{SCE}=0$, with incident laser at 6471 Å.

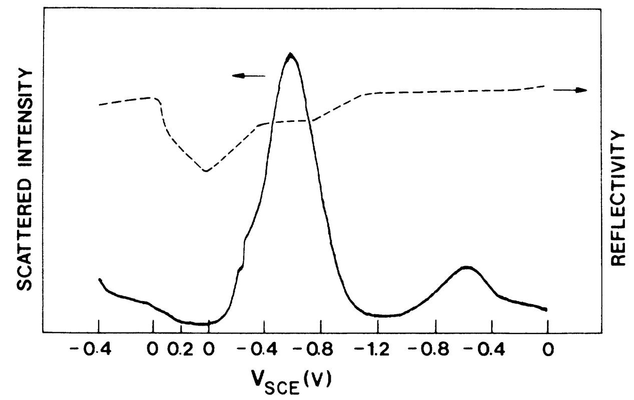

FIG. 5. Continuous trace of pyridine SERS line intensity at 1008 cm^{-1} (solid line) and surface reflectance of the electrode (dashed line) during triangular ramps of the electrode potential at room temperature in (0.05*M* pyridine)/(0.1*M* KCl)/water/Ag electrode system. Ramp rate at 5 mV_{SCE}/sec in the range of potential: $V_{SCE}=0$ to $V=-1.2$ V_{SCE} and back to $V_{SCE}=0$, with laser excitation at 5309 Å.

observed as long as the electrode potential is kept higher (less negative) than $V=-1.4$ V_{SCE}.

In Fig. 5, we see that the Ag electrode shows at room temperature a substantial gain in the surface reflectance at $V=-0.75$ V_{SCE}. This gain in the surface reflectance along with the irreversible loss in SERS intensity, observed at $V=-0.75$ V_{SCE} of the non-Faradaic region where large-scale roughness of the surface remains unchanged, suggests that adatoms do affect the surface reflectance as well as the SERS intensity. The Ag-adatom diffusion in the silver-electrode electrochemical system at room temperature has been believed to cause the irreversible loss of SERS intensity at $V=-0.75$ V_{SCE}.[9,10]

The Cu-adatom effect was also found in the ultrahigh vacuum (UHV) system,[8] where irreversible loss of SERS intensity was observed at $T\simeq 250$ K. Our observation of the irreversible loss of SERS intensity at above $T\simeq 313$ K (40 °C) in the Cu-electrode electrochemical system seems to suggest that Cu adatoms form a surface complex in combination with pyridine, Cl^-, water molecules, etc., to become less mobile than the bare Cu adatoms in the UHV systems. In the UHV system, Ag adatoms become diffusive at $T\simeq 210$ K while Cu adatoms become diffusive at higher temperature of $T\simeq 250$ K.[8] This observation is compatible with the fact that the surface binding energy of Cu atoms is larger than that of Ag atoms.[18] It may be possible that the irreversible loss of SERS intensity may not be observable in the Ag electrode system if the solution temperature can be lowered well below the room temperature.

CONCLUSION

The SERS system of (0.05*M* pyridine)/(0.1*M* KCl)/water/Cu has the instability of the surface adatoms at temperatures above 40 °C and electrode potential below -1.45 V_{SCE}. Surface reflectance of the SERS electrode increases during the irreversible loss of SERS intensity associated with the adatomic diffusions in the non-Faradaic region where we have no change in the large scale roughness of the surface. This surface reflectance dependence on the adatom surface concentration should be differentiated with the Rayleigh scattering enhancement and reflectance dependence on the degree of excitation of surface plasmons associated with the large-scale roughness of the surface. Our experimental result, the instability of the surface atoms on the copper electrode at elevated temperatures, indicates that some microscopic features of the surface reconstruction may be involved in the SERS mechanism. This does not necessarily selectively support the chemical or electrodynamic resonance effect in SERS since adatoms are important in both chemical effects and small cavity formations.

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[1] *Surface Enhanced Raman Scattering,* edited by R. K. Chang and T. E. Furtak (Plenum, New York, 1982).

[2] A. Otto, in *Light Scattering in Solids IV,* Topics in Applied Physics, Vol. 54, edited by M. Cardona and G. Güntherodt (Springer, Berlin, 1984), p. 289.

[3] R. K. Chang and B. L. Laube, Crit. Rev. Solid State Mater. Sci. **12**, 1 (1984).

[4] M. Moskovitz, Rev. Mod. Phys. **57**, 783 (1985).

[5] B. Pettinger, A. Tadjeddine, and D. M. Kolb, Chem. Phys. Lett. **66**, 544 (1979).

[6] S. Ushioda and Y. Sasaki, Phys. Rev. B **27**, 1401 (1983).

[7] S. H. Macomber and T. E. Furtak, Solid State Commun. **45**, 267 (1983).

[8] U. Erturk, I. Pockrand, and A. Otto, Surf. Sci. **131**, 367 (1983).

[9] J. F. Owen, T. T. Chen, and R. K. Chang, Surf. Sci. **131**, 195 (1983).

[10] D. H. Ha, S. K. Lee, and J. J. Kim, Chem. Phys. Lett. **141**, 104 (1987).

[11] H. Chew and M. Kerker, J. Opt. Soc. Am. B **2**, 1025 (1985).

[12] H. Seki *et al.*, Surf. Sci. **158**, 254 (1985).

[13] E. V. Albano *et al.*, Phys. Rev. Lett. **51**, 2314 (1983).

[14] H. Seki and T. J. Chuang, Chem. Phys. Lett. **100**, 393 (1983).

[15] L. Morel and B. Pettinger, Solid State Commun. **43**, 315 (1982).

[16] J. Billmann, G. Covacs, and A. Otto, Surf. Sci. **92**, 153 (1980).

[17] A. Otto, J. Billmann, J. Eickmanns, U. Erturk, and C. Pettenkofer, Surf. Sci. **138**, 319 (1984).

[18] G. A. Somorjai, *Chemistry in Two Dimensions: Surfaces* (Cornell Univ. Press, London, 1981).