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Influence of Chemisorption of 2-Propanethiol on the Electrical Properties of Silver Oxide Compaction

Naoto Yamamoto,* Shoichiro Tonomura, Tsugufumi Matsuoka,
Takashi Amamiya, and Hiroshi Tsubomura
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

(Received September 18, 1980)

The work function of silver oxide (Ag_2O) decreased by as much as 0.8 eV on exposure to 2-propanethiol [$(CH_3)_2CHSH$]. The change in work function was irreversible at room temperature, and proportional to the amount of thiol in case where the partial pressure is low, but reversible at 200 °C. The conductivity of the Ag_2O disk showed no substantial change by exposure to thiol. From the infrared absorption spectral studies, it was found that the thiol reacted with the silver oxide forming a $(CH_3)_2CH–S–Ag$ group on the surface. The relationship between the work function and the chemical processes occurirng at the solid surface is discussed.

Recently, the employment of semiconductors for specific detection of gases taking advantage of the change in electric conductivity has been attempted by many authors.[1–5] Concerning the mechanism in such systems, it is essentially important to clarify how the electrical properties of the semiconductors are correlated with chemical processes occurring at the solid-gas interface. From this point of view, we have studied the influence of gases on the surface potentials and other electrical properties of metals and metal-semiconductor assemblies.[6] The surface potentials have also been studied for electrodes chemically modified with antibodies or enzymes. The change in electrode potentials by specific reactions between biological substances at the electrode-solution interface[7,8] has been found to be capable of serving as a sensitive device for analysis of these substances.

In this work, the effect of thiol gas on the electrical properties of silver oxide in the form of compaction (compressed powder) or thin film has been investigated. It has been found that the conductivity is insensitive, but the surface potential is very sensitive to the gas. The results are discussed in relation with informations obtained on the chemical processes on the solid surface from infrared absorption measurements.

Experimental

Materials. Copper plate, 99.9% pure, 1 mm thick, was used as the reference electrode, or the substrate for evaporated metal films. The purities of Ag, Fe, Ni, Pd, and Al used were higher than 99.9%. 2-Propanethiol gas used was evolved from the liquid 98% pure 2-propanethiol, obtained from Tokyo Kasei Kogyo Co. The silver oxide powder 99.9% pure, having the grain size of about 0.5 μm, was obtained from Kishida Chemical Co.

Procedure. The contact potential of the silver oxide samples against copper was measured by use of a vibrating capacitor method.[9] The experimental setup is schematically shown in Fig. 1. The metal to be studied, Ag, Fe, Ni, Pd, or Al, was evaporated on a Cu plate at 2×10^{-5} Torr (1 Torr$=$133.322 Pa). Silver oxide powder, 1.0 g in weight, was compressed at 150 kg/cm^2 into a disk form and the disk was attached onto a Cu plate with silver paste.

The reference electrode, a semicircular Cu plate 15 mm in radius, was rotated with a speed of 30 Hz by use of a synchronous motor. The space between both electrodes was adjusted with a micrometer to *ca.* 0.2 mm. The ac current arising from the capacity change between the electrodes was measured by use of a Teledyne Philbrick 1702 parametric amplifier and an NF LI-573 lock-in-amplifier. The contact potential between these electrodes was determined by employing the null current method with the aid of a potentiometer. The electrodes were kept in a box, 7 l in capacity. For electric conductivity measurements, gold was vacuum-evaporated onto the silver oxide disk as shown in Fig. 2.

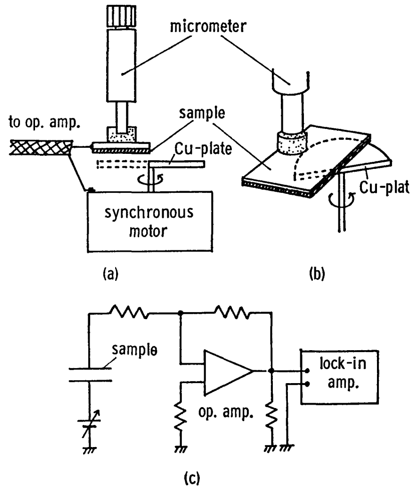

Fig. 1. Schematic representation of the experimental setup for contact potential measurements: (a) a front view and (b) a bird's-eye view. (c) The electric circuit.

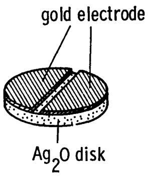

Fig. 2. The Ag_2O disk used for measuring its electric conductivity.

Infrared spectra were measured by use of a JEOL JIR 10 Fourier transform infrared spectrometer. Silver film to be measured was prepared by vacuum-deposition onto a NaCl disk, the transmittance of the film being 40% at 600 nm.

Results and Discussion

Surface Potential of Ag_2O. The average contact potential difference between an Ag_2O disk and a

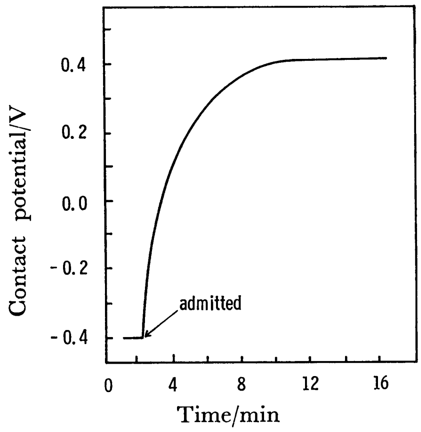

Fig. 3. The response in the contact potential of the Ag_2O disk to 2-propanethiol at room temperature.

copper reference electrode was found to be -0.40 V, when measured in air, indicating that the work function of Ag_2O is 0.40 eV larger than that of the copper electrode. The copper electrode is presumably covered with a thin copper oxide film in air and the absolute value of its work function cannot be determined directly by the capacitor method.

Figure 3 shows the change in the contact potential caused by admission of 5.0×10^{17} molecules of 2-propanethiol, into the box. The potential increased from -0.40 V to $+0.40$ V and became constant after about 10 min. No change in potential was observed by dissipating the gas into open air. When a disk previously exposed to thiol was heated at 200 °C in air, the potential decreased and returned to the value of unexposed Ag_2O, -0.40 V. These changes in potential are obviously due to chemisorption of the thiol on the Ag_2O surface.

It was confirmed from the following experiment that the work function of the copper reference did not change by the introduction of 2-propanethiol: First, the thiol gas was introduced into the box. The contact potential of the Ag_2O disk against the copper electrode changed as shown above. After that, the gas was removed from the box and only the Ag_2O disk was replaced by a new Ag_2O disk. The contact potential between the new disk and the copper electrode exposed to the gas showed the same value as that obtained between fresh Ag_2O and Cu electrodes in air. On replacement of the disk by a new copper plate, the contact potential was almost zero between the new and the gas exposed copper electrode. These experimental results indicate that the change in surface potential of Cu plate by exposure to thiol is negligible.

The induced potential is plotted against the amount of 2-propanethiol admitted into the box (Fig. 4). In the low partial pressure region, it is proportional to the amount of thiol introduced, but gradually saturated at higher pressure region.

The work function, ϕ, of Ag_2O, corresponding to the energy required to transfer an electron from its Fermi level to vacuum, is determined from our experiment in air as 5.6 eV, taking the work function of copper to be 5.2 eV that was obtained in the presence of oxygen.[10,11] Before chemisorption, the potential for an electron near the disk surface may be described as shown in Fig. 5(A)[12] by taking account of the image force. The chemisorbed thiol will form an electric dipole on the Ag_2O surface (Fig. 5(B)). The potential can, then, be expressed by the superposition of the image force and electric double layer potentials as illustrated, lowering the vacuum level outside the Ag_2O surface by $\Delta\phi=0.8$ eV at its maximum.

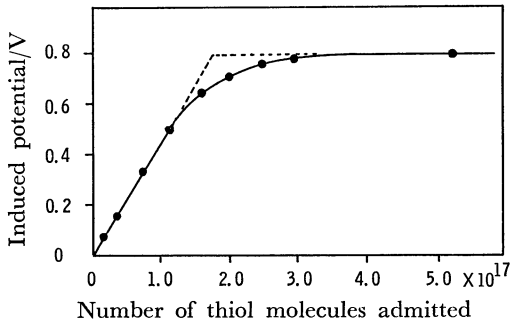

Fig. 4. The induced change of potential of the Ag_2O disk against the amount of 2-propanethiol introduced.

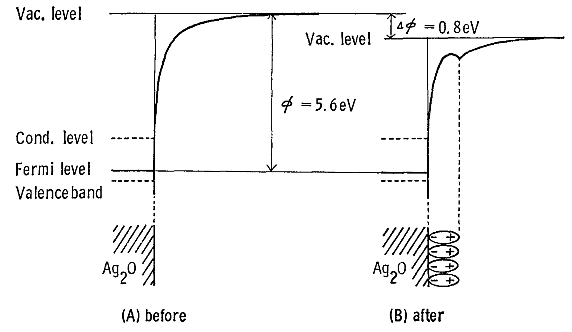

Fig. 5. Schematic energy diagrams of the Ag_2O disk near the surface before and after the introduction of 2-propanethiol gas.

The electrical behavior of a silver film against the gas introduction was almost similar to that of Ag_2O disk. The contact potential difference of the evaporated silver film was -0.25 eV against a copper reference electrode in air. The magnitude of surface potential change was 0.45 eV by admission of 5.0×10^{17} molecules of 2-propanethiol. The surface of the Ag film is presumably covered with a thin film of the oxide in air, and therefore the chemisorption mechanism on the film is essentially the same as on the Ag_2O disk.

As described earlier the changes in surface potential resulting from the reaction of 2-propanethiol can be explained by taking account of the induced dipole moment, $\Delta\mu$, by the chemisorption. The electrical potential, $\Delta\phi$, owing to the double layer formation is expressed by the following equation.

$$\Delta\phi = -\Delta\mu\cdot N/\varepsilon_0 \tag{1}$$

Where N is surface density of the chemisorbed thiol and ε_0 is permittivity of vacuum. An 2-propanethiol molecule has a cross section of about 26 Å^2. Then, taking $\Delta\phi=0.8$ V, the highest value obtained, and $N=3.7\times10^{18}$ m^{-2}, calculated from the closest array

TABLE 1. THE ASSIGNMENT OF IR ABSORPTION BANDS (in cm^{-1}) OBTAINED FOR 2-PROPANETHIOL ADSORBED ON THE Ag FILM AND THE Ag_2O DISK

$(CH_3)_2CHSH$		$(CH_3)_2CHSAg$	$(CH_3)_2CHSH$ Vapor[a]	Assignment
Ads. on Ag_2O	Ads. on Ag			
1037	1041	1045	1063	CH_3 rock
1145	1146	1150	1161	CH_3 rock
1226 1240	1236	1232	1244 1266	CH wag
	1377	1380	1389	CH_3 bend(sym)
	1456	1440 1456	1448	CH_3 bend(unsym)
			2572	SH stretch
	2850	2860	2867	CH_3 stretch(sym)
	2923	2920	2909 2927	CH stretch
	2952	2050	2967	CH_3 stretch(unsym)

a) Taken from Ref. 14.

of thiol molecular layer on the surface, $\Delta\mu$ is calculated to be 0.57 D, which seems to be a reasonable value in view of the dipole moment of 2-propanethiol molecule, 1.64 D, in liquid state.[13]

Crystalline Ag_2O has a body centered cubic structure, where four silver atoms exist in a unit cell and its lattice constant is 4.72 Å. If the unit cells are assumed to align regularly at the surface, the cross-sectional area of 2-propanethiol is comparable to that of a unit cell of Ag_2O, so that approximately one of the four silver atoms in the cell can react with the thiol.

As up to *ca.* 4.0×10^{17} molecules of 2-propanethiol is capable of changing the disk surface potential, the actual area of the disk surface is estimated to be 0.1 m^2 under the assumption of monomolecular chemisorption. The radius of the grain of Ag_2O powder is *ca.* 0.25 μm, so that the total surface area of the powder of 1 g is calculated to be *ca.* 1.7 m^2 before making the disk. Such a decrease in the surface area seems reasonable as a result of compression in the process of disk formation.

The Pd electrode shows very high response to hydrogen gas as described in a previous paper.[6] The Ag_2O electrode was, however, insensitive to hydrogen or carbon monoxide, but showed a small response to water and carbon dioxide. The electrode of Ni or Al had no response to the thiol up to the concentration of 2.5 ppm. The potential of the electrode of Fe changed by 23 mV with 0.3 ppm thiol.

Electrical Resistance of Ag_2O. The electrical resistance of an Ag_2O disk in a 1.0 mm gap between gold electrodes (Fig. 2) was *ca.* 6.5 MΩ in air at room temperature. No change in electrical resistance was observed as 1.0×10^{18} molecules of 2-propanethiol was introduced into the box. This fact indicates that the conductivity is mostly through the bulk of Ag_2O disk, and is not affected by the chemical processes occurring at the solid surface.

Infrared Spectra of 2-Propanethiol Adsorbed on Ag and Ag_2O. Infrared absorption spectrum was measured for the thiol adsorbed on an Ag_2O disk, 0.1 mm thick, and the band positions observed are shown in column 1 of Table 1. The IR spectrum measured for thiol adsorbed on a silver film evaporated on a sodium chloride disk (Fig. 6) gives more clear bands than on the Ag_2O disk. The spectrum was taken from fifty sweeps of transmittance measurements at room temperature. The negative absorption at around 2349 cm^{-1} is due to carbon dioxide present in air. Even after allowing to stand for 8 d in contact with air, the film showed almost the same spectrum as that in Fig. 6. The absorption peak positions are also listed in column 2 of Table 1. These assignments given in the last column in Table 1 were based on the spectral data obtained for gaseous 2-propanethiol by Smith and Devlin.[14]

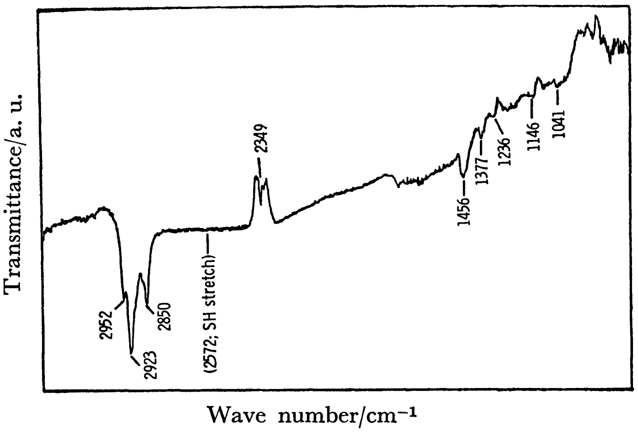

Fig. 6. Infrared absorption spectrum of Ag film exposed to the thiol gas.

The adsorbed thiol on the silver film shows several bands ascribable to CH_3 symmetric and unsymmetric stretchings at 2850 and 2952 cm^{-1}, CH wagging at 1236 cm^{-1} and CH stretching at 2923 cm^{-1}, but does not show any absorption at 2572 cm^{-1} where gaseous 2-propanethiol shows a band assigned to the S–H stretching. It was also confirmed that the infrared spectrum of silver 2-propanethiolate powders synthesized by the reaction of 2-propanethiol and $AgNO_3$ in solution is essentially the same as that shown in Fig. 6 (column 3 of Table 1). These results indicate that most of the chemisorbed molecules are dissociatively adsorbed as follows,

$$\mathrm{RSH} \longrightarrow \mathrm{RS}\cdots\overset{|}{\underset{|}{\mathrm{Ag}}} + (\mathrm{H}).$$

It can thus be concluded that the potentiometric response of the silver oxide disk arises predominantly from the surface potential change due to the chemisorption, and that the electric property of bulk is little affected by the change of the surface structure.

References

1) T. Seiyama and S. Kagawa, *Anal. Chem.*, **38**, 1069 (1966).

2) H. A. Himpler, S. F. Brand, and M. J. D. Brand, *Anal. Chem.*, **50**, 1623 (1978).

3) P. J. Shaver, *Appl. Phys. Lett.*, **11**, 255 (1967).

4) H. Obayashi, Y. Sakurai, and T. Gejo, *J. Solid State Chem.*, **17**, 299 (1976).

5) H. Windischmann and P. Mark, *J. Electrochem. Soc.*, **126**, 627 (1979).

6) N. Yamamoto, S. Tonomura, T. Matsuoka, and H. Tsubomura, *Surf. Sci.*, **92**, 400 (1980).

7) N. Yamamoto, Y. Nagasawa, S. Shuto, M. Sawai, T. Sudo, and H. Tsubomura, *Chem. Lett.*, **1978**, 245; N. Yamamoto, Y. Nagasawa, M. Sawai, T. Sudo, and H. Tsubomura, *J. Immunol. Methods*, **22**, 309 (1978).

8) N. Yamamoto, T. Nagasawa, S. Shuto, and H. Tsubomura, *Clin. Chem.*, **26**, 1569 (1980).

9) J. C. Riviere, "Solid State Surface Science," ed by M. Green, Marcel Dekker, New York, N. Y. (1969), Vol. 1, Chap. 4.

10) W. F. Krolikowski and W. E. Spicer, *Phys. Rev.*, **185**, 882 (1969); S. Trasatti, "Advances in Electrochemistry and Electrochemical Engineering," ed by C. W. Tobias and H. Gerischer, John Wiley & Sons, Inc., New York, N. Y. (1977), Vol. 10, p. 213.

11) F. C. Tompkins, "The Solid-Gas Interface," ed by E. A. Flood, Marcel Dekker, Inc., New York, N. Y. (1967), Chap. 25.

12) The energy gap between the conduction band and the valence band of Ag_2O is reported to be 1.1 to 1.5 eV [See E. Fortin and F. L. Weichman, *Phys. Status Solidi*, **5**, 515 (1964)], although the detailed nature of the compound as a semiconductor has not been clarified.

13) S. Mathias and E. de Carvalho Filho, *J. Phys. Chem.*, **62**, 1427 (1958).

14) D. Smith, J. P. Devlin, and D. W. Scott, *J. Mol. Spectrosc.*, **25**, 174 (1968).