ELLIPSOMETRIC STUDIES OF OXYGEN ADSORBED ON SILVER FILMS

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Résumé - L'adsorption d'oxygène sur des couches minces d'Argent déposées par
évaporation a été étudiée à 295 et 77 K par ellipsométrie et par mesures de
résistance. La constante diélectrique obtenue pour l'oxygène adsorbé sous
forme atomique, à 1152 nm, est $\tilde{\varepsilon}_1$ = - 1,8 - 3,5i à 295 K et - 2,0 - 4,0i à
77 K ; ces valeurs sont bien interprétées par la théorie de Bennett et Penn
qui décrit le couplage entre l'oxygène adsorbé et les électrons de conduction.
Les valeurs $\delta\Delta$ et $\delta\psi$ observées à λ = 633 nm indiquent l'existence d'une cou-
che d'interface induite. La constante diélectrique de l'oxygène adsorbé sous
forme moléculaire à 77 K est réelle et égale à ε_1 = 1,8.

Abstract - Adsorption of oxygen on evaporated silver films is studied at
295 and 77 K by means of ellipsometry and resistance measurements. The dielec-
tric constant of atomically adsorbed oxygen obtained at λ = 1152 nm is $\tilde{\varepsilon}_1$ =
-1.8 - 3.5i at 295 K and -2.0 - 4.0i at 77 K, which are well understood by the
Bennett and Penn theory describing coupling between adsorbed oxygen and con-
duction electrons. Observed $\delta\Delta$ and $\delta\psi$ values at λ = 633 nm indicate the exi-
stence of an induced interface layer. The dielectric constant of molecularly
adsorbed oxygen at 77 K is found to be real as ε_1 = 1.8.

Oxygen is atomically adsorbed on polycrystalline silver surfaces at room temperature
while at 77 K it seems to be adsorbed atomically at early stage of adsorption and then
weakly and molecularly |1-3|. We intend in this paper to compare ellipsometric respon-
se of adsorbed oxygen at 295 K with that at 77 K. A few other groups have studied this
system at room temperature by means of ellipsometry using light wavelengths of 633 nm
or shorter |4-6|. Our light source was a He-Ne laser of λ = 1152 nm, where the metal
dielectric constant can be described by an extended Drude equation including the ano-
malous skin effect. As well we used another He-Ne laser of 633 nm to compare our re-
sults with literature work. Evaporated thin films were considered to be advantageous
for determining the life time of conduction electrons and Fuch's specularity parameter
from resistivity measurements. We measured changes in the ellipsometric angles $\delta\Delta$ and
$\delta\psi$ as a function of oxygen coverage, which were converted into the complex dielectric
constants of adsorbed oxygen. They were found to be different from those of liquid or
gas phase oxygen.

I - EXPERIMENTS

Experimental details are given elsewhere |7,8|. A null method ellipsometer (Rudolph
43603-200E) was used in the PSCA arrangement. Samples were polycrystalline and conti-
nuous films deposited on glass substrates in UHV conditions. Spectrally pure silver
was evaporated from a tungsten helix heater onto the substrate which was kept at am-
bient temperature. The thickness D of the films was in the range of 25 to 50 nm, which
was determined by atom absorption spectroscopy. The resistance of the films was measu-
red by a so-called four electrode method during evaporation, annealing and gas admis-
sions. The gas dose was provided by breaking the seals of ampoules filled with O_2 gas
of 99.999 % purity. The adsorbed amount of O_2 was determined by monitoring increments
of the resistance using calibration curves obtained for spherical glass cells |8|.
Since variations in Δ and ψ due to O_2 adsorption were small, we evaluated them with the
help of computer analysis. Details of the method are given elsewhere |9|.

II - RESULTS

Electron micrographs show that a continuous film structure with a preferred (111) orientation is formed for $D \gtrsim 15$ nm. The films become smoother with increasing D. Observed Δ and ψ values of the films without adsorbate are converted into dielectric constant $\tilde{\varepsilon}_2$ by computer calculations of a two layer system including the metal films and the glass substrate with refractive index of 1.48. Obtained dielectric constant is $\tilde{\varepsilon}_2 = (-75 \pm 4) - (2.5 \pm 0.5)i$ at $\lambda = 1152$ nm while the Drude equation gives $\tilde{\varepsilon}_2 = -72.5 - 2.34i$ with $\varepsilon_b = 2.5$ being the core electrons contribution $|10|$. At $\lambda = 633$ nm we obtained $\tilde{\varepsilon}_2 = (-22 \pm 2) - (0.4 \pm 0.2)i$ while the Drude value is $\tilde{\varepsilon}_2 = -19.5 - 0.48i$. Thus the observed $\tilde{\varepsilon}_2$ values are well described by the Drude theory.

Solid curves in Fig. 1a show the coverage dependence of the ellipsometrical parameters $\delta\Delta$ and $\delta\psi$ defined as

$$\delta\Delta = \Delta(\Theta=o) - \Delta(\Theta), \qquad \delta\psi = \psi(\Theta=o) - \psi(\Theta), \tag{1}$$

where Θ is the degree of oxygen coverage. It was ascertained that $\delta\Delta$ and $\delta\psi$ are independent of film thickness D when it is larger than 25 nm. If an adlayer is transparent for an incident light, a simple stratified layer model predicts $|11|$:

$$\delta\Delta = C(\lambda)\alpha\Theta/\lambda \qquad \delta\psi \leq 0, \tag{2}$$

where α is the atomic polarizability of the adsorbate and $C(\lambda)$ is a function of λ, incident angle of the light and adsorbent optical properties. Obviously the results of Fig. 1a are very inconsistent with eq. (2), so that we may need an induced interface layer and/or a complex dielectric constant of adsorbed oxygen to explain the data. The 6.4 % increase in the resistance seems to indicate that oxygen atoms are not adsorbed by silver for O_2 pressures smaller than 1.3 Pa used in the present experiments (see Fig. 1b).

At 77 K observed changes in $\delta\Delta$ and $\delta\psi$ values are $\delta\Delta = 0.28^0$, $\delta\psi = 0.07^0$ at $\lambda = 1152$ nm and $\delta\Delta = 1.0^0$, $\delta\psi = -0.22^0$ at 633 nm for the coverage of $N_{ad} = 4.0 \times 10^{14}$ molecules/cm^2. At low coverages, variations in $\delta\Delta$, $\delta\psi$ and δR are similar to those in Fig. 1 though $\delta\psi$ at 633 nm is largely negative. At high coverages $\delta\Delta$ is almost linear and $\delta\psi$ is constant. A Characteristic feature is that $\delta\Delta$ does not tend to saturate at high coverages unlike that at 295 K, possibly due to weak adsorption of molecular oxygen. The maximum change in the resistance $\delta R/R$ at 77 K is 7.2. % for a Ag film of D = 42 nm.

III DISCUSSION

The surfaces of the evaporated Ag films are treated to be flat, which is an admissible assumption because their bumpiness is much smaller than λ. Furthermore, we now take into account that the glass substrate only influences the absolute values of Δ and ψ but is ineffective for $\delta\Delta$ and $\delta\psi$ when the thickness of Ag films is larger than the skin depth $\delta_s = 21$ nm. Applying the model of Fig. 2b, $\delta\Delta$ and $\delta\psi$ are expressed in simply analytical forms by the linear approximation under the condition of $d_{ad}/\lambda \ll 1$. Non-classical expressions of $\delta\Delta$ and $\delta\psi$ which include the non-local effects were given in a previous paper $|10|$:
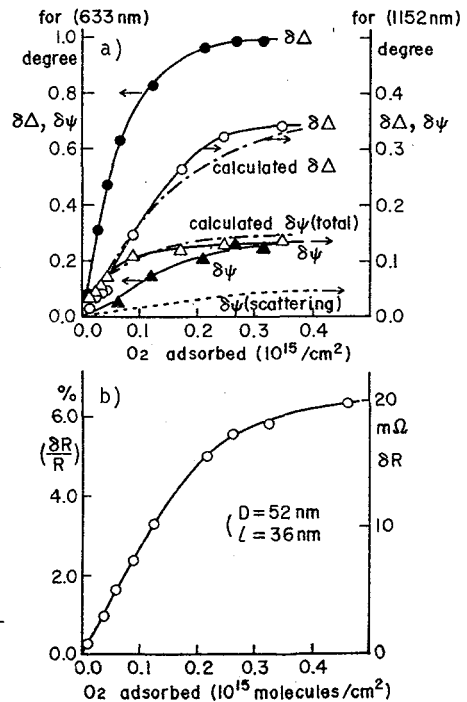
Fig. I Changes in ellipsometric angles $\delta\Delta$, $\delta\psi$ at 1152 nm (o, $\triangle$) and 633 nm ($\bullet$, $\blacktriangle$) and resistance of Ag film δR plotted with the coverage of adsorbed oxygen at 295 K. Dotted curve shows calculated $\delta\psi$ which arises from the p parameter effect. Simulations of $\delta\Delta$ and $\delta\psi$ at 1152 nm are given by chained curves.

$$\delta\Delta = \frac{-4\pi d_{ad} n_0 \cos\phi_0}{\lambda} \times Re \ |Fn| \tag{3a}$$

$$\delta\psi = \sin 2\psi \ \frac{2\pi d_{ad} n_0 \cos\phi_0}{\lambda} \times Im \ |Fn| \tag{3b}$$

$$Fn = (\frac{\tilde{\varepsilon}_1 - \tilde{\varepsilon}_2}{\tilde{\varepsilon}_0 - \tilde{\varepsilon}_2}) \ \{\frac{1 - \varepsilon_0(1/\tilde{\varepsilon}_1 + 1/\tilde{\varepsilon}_2)\sin^2\phi_0 + \tilde{\varepsilon}_1 Q/(\tilde{\varepsilon}_1 - \tilde{\varepsilon}_2)}{1 - \varepsilon_0(1/\varepsilon_0 + 1/\tilde{\varepsilon}_2)\sin^2\phi_0 + \varepsilon_0 Q/(\varepsilon_0 - \tilde{\varepsilon}_2)} - 1\} \tag{4}$$

$$Q = 2\gamma(\tilde{\varepsilon}_2 - \varepsilon_0 \sin^2\phi_0)^{1/2} + \tilde{\varepsilon}_2\gamma^2, \quad \gamma = \frac{1}{(K_\ell)_n} \ (\frac{\varepsilon_0}{\tilde{\varepsilon}_2} - \frac{\varepsilon_0}{\tilde{\varepsilon}_1})\sin^2\phi_0 \tag{5}$$

where definitions of variables and dielectric constants are given in Fig. 2. $(K_\ell)_n$ is the normal component of longitudinal wave vector $|12,13|$. When γ is small, then $\delta\Delta$ and $\delta\psi$ reduce to the classical forms. Eqs. 3 are the expressions at $\Theta = 1$. Since the observed $\delta\Delta$ and $\delta\psi$ values are non-linear with coverage, the coverage curves are analyzed with the help of Lorentz-Lorenz equation by substituting $\tilde{\varepsilon}_1$ in eqs. 4 and 5 by $\tilde{\varepsilon}_1(\Theta)$ according to $|10|$
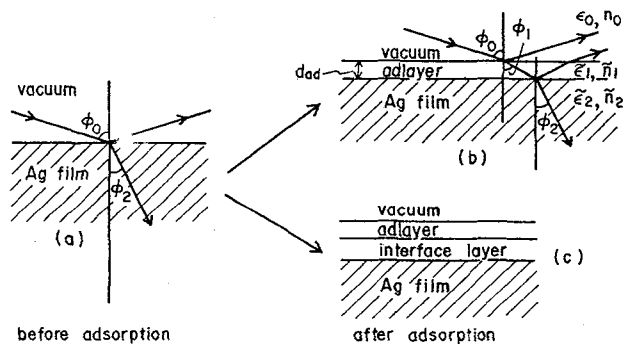

Fig. 2 Stratified layer model of oxygen adsorption on Ag films and definitions of variables.

$$\frac{\tilde{\varepsilon}_1(\Theta) - 1}{\tilde{\varepsilon}_1(\Theta) + 2} = \Theta(\frac{\tilde{\varepsilon}_1 - 1}{\tilde{\varepsilon}_2 + 2}) \tag{6}$$

The dielectric constant of Ag is given by the extended Drude equation including anomalous skin effects $|10,14|$ as

$$\tilde{\varepsilon}_2 = \{1 - (\frac{\omega_p}{\omega})^2\} - i \ (\frac{\omega_p}{\omega})^2 \cdot \frac{1}{\omega\tau_{op}} \ \{1 + \frac{3}{8} (1-p) (\frac{\ell_{op}}{\delta_s}) (1 - (\frac{\omega}{\omega_p})^2)^{3/2}\}, \tag{7}$$

with

$$1/\tau_{op} = 1/\tau_{st} + 1/\tau_{ee} \quad , \tag{8}$$

where ω and ω_p are frequencies of incident light and the plasmon, respectively, δ_s is the skin depth, p is the Fuchs specularity parameter, $\tau_{op} = v/l_{op}$ is the optical life time of conduction electrons, τ_{st} is the static life time calculated from observed resistance of Ag films and τ_{ee} is the life time determined from electron-electron collisions $|15|$ which are important when ω is large and the Fermi surface is non-spherical or surface scatterings of conduction electrons are effective.

Since the films are assumed to be flat, the resistance is analyzed by the Fuchs-Sondheimer theory. Observed resistance changes are approximately expressed by $|10|$:

$$(\frac{\delta R}{R}) = (\frac{\delta\rho}{\rho}) \simeq \frac{\delta p}{2(\frac{8}{3}\frac{D}{l} - 1)} \tag{9}$$

from which we calculated δp by using observed ($\delta R/R$) values. D/l is 1.4 at 295 K, thus we obtain δp = 0.36. After numerical calculations we found that this leads to $\delta \psi$ = 0.05°, which is illustrated by the dotted curve in Fig. 1. The calculation reveals that δp influences only little $\delta \Delta$. For the 77 K results, similar conclusions hold.

Following the above procedure we simulated observed $\delta \Delta$ and $\delta \psi$ curves with parametrizing $\tilde{\epsilon}_1$ and d_{ad}, but d_{ad} is fixed around 0.2 nm for atomic oxygen and around 0.35 nm for molecular oxygen. At 295 K adsorbed oxygen is atomic. Simulation curves of $\delta \Delta$ and $\delta \psi$ are shown in Fig. 1 at 1152 nm with best fitted $\tilde{\epsilon}_1$ value being $\tilde{\epsilon}_1$ = -1.8 - 3.5i. On the other hand, at 633 nm none of $\tilde{\epsilon}_1$ values can interpret the coverage curves, in particular with respect to the steep rise of $\delta \Delta$ at the early coverage. Therefore, we conclude that at 633 nm the formation of an induced interface layer must be taken into account, i.e. model (c) rather than model (b) should be applied. This conclusion implies that dielectric constant of the interface layer depends strongly on λ like $\tilde{\epsilon}_2$ of Ag. In model (c), determination of $\tilde{\epsilon}_1$ is impossible because of many unknown parameters.

Along the same lines we analyzed our low coverage data at 77 K. We simulated coverage curves of $\delta \Delta$ and $\delta \psi$ and arrived at the same conclusion that model (b) explains well the result at 1152 nm with simulation parameters of $\tilde{\epsilon}_1$ = -2.0 - 4.0i and d_{ad} = 0.2 nm, but does not explain at all the result at 633 nm, while model (c) does. Observed changes in ellipsometric angles in the high coverage range are $\delta \Delta$ = 0.15°, $\delta \psi$ = -0.02° at 1152 nm and $\delta \Delta$ = 0.40°, $\delta \psi$ = 0.00° at 633 nm, which can be interpreted by weakly adsorbed molecular oxygen with $\tilde{\epsilon}_1$ = 1.8 - 0.0i and d_{ad} = 0.35 nm.

IV CONCLUSIONS

Dielectric constants of atomic oxygen on silver at 1152 nm are $\tilde{\epsilon}_1$ = -1.8 - 3.5i at 295 K and $\tilde{\epsilon}_1$ = -2.0 - 4.0i at 77 K. Such complex dielectric constants with negative real parts were predicted by the Bennett and Penn theory |16| describing possible resonant bonds between adsorbates and conduction electrons. UPS spectra of adsorbed oxygen on silver |3,17| show two peaks at 8.0 and 12 eV from E_f which lie below the conduction band, and a peak at 3.2 eV in the sp conduction band. Dielectric properties of adsorbed oxygen may reflect the covalent nature of electrons at 8.0 eV and the metallic nature of electrons at 3.2 eV. The existence of induced interface layer depends on λ of incident light. Non-local effects in the linear approximation are as small as 6 % at λ = 633 nm and negligible at 1152 nm.

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