LE JOURNAL DE PHYSIQUE - LETTRES

J. Physique — *LETTRES* 44 (1983) L-99 - L-104

1^{er} FÉVRIER 1983, PAGE L-99

Classification
Physics Abstracts
68.60

Roughening of a smooth cold Ag surface by Ag overlayers studied by differential reflectivity

T. Lopez-Rios, Y. Borensztein and G. Vuye

Laboratoire d'Optique des Solides (*), Université Pierre et Marie Curie,
4, place Jussieu, 75230 Paris Cedex 05, France

(Reçu le 21 septembre 1982, accepté le 16 décembre 1982)

Résumé. — Les variations de la réflectivité, dues au dépôt de faibles quantités d'Ag (10 à 200 Å) sur un substrat lisse d'Ag polycristallin et refroidi à 140 K, sont étudiées par la mesure de la réflectivité différentielle. Nous analysons les modifications des propriétés optiques causées par la rugosité à la surface, ainsi que le recuit des couches d'argent. Nous discutons ensuite de leur rapport avec la diffusion Raman « géant » (SERS).

Abstract. — The results of an investigation by differential reflectivity of the reflectivity change due to the deposition of small amounts of Ag (10 to 200 Å) on a cold (140 K) polycrystalline smooth Ag substrate are presented. The modifications of the optical properties due to the roughening of the surface are analysed, the annealing of the deposited Ag overlayers is investigated and their relationship with Surface-Enhanced Raman Scattering (SERS) is discussed.

A large amount of experimental work has been devoted to Surface-Enhanced Raman Scattering (SERS) performed on metallic surfaces prepared by deposition on cold substrates. The structure and surface roughness of these « cold » films is poorly known. Since many years it has been known that « cold » films of silver and gold display an anomalous optical absorption band, which disappears with annealing [1, 2] and which has been attributed to bulk, mainly grain boundaries, defects [3]. More recently, Moskovits *et al.* [4, 5] and Otto *et al.* [6] working on silver, have found a shift of the spectral position of the anomalous absorption band towards higher energies during annealing. Until now neither the optical properties of such films nor the relationship between these properties and SERS are well understood. Moreover, there is some discussion concerning the role of atomic-scale roughness generated by very thin deposits of Ag on flat cold Ag surfaces [7, 8]. For instance, Wood [7] did not find any detectable Raman signal for pyridine on silver deposits thinner than about 150 Å.

We present here the results of an investigation by differential reflectivity of the change due to the deposition of small (10 to 200 Å) amounts of Ag on a cold (140 K) polycrystalline Ag substrate.

(*) E.R.A. 462.

We analyse the modification of the optical properties due to the early roughening of the surface, we investigate the annealing of the deposited Ag overlayers and we discuss their relationship with SERS.

1. Experiments. — The samples were prepared by Joule-effect heating of Ag in an ultrahigh vacuum chamber equipped with a Leed-Auger spectrometer for surface analysis. The pressure was kept below 10^{-9} torr during the silver deposition and during the measurements. The fused silica substrate is maintained in contact with a liquid nitrogen holder, which can lower the substrate temperature down to 140 K. The thickness of the metallic deposits is controlled with a 5 MHz quartz crystal microbalance calibrated by thickness measurements using grazing incidence X-ray interferometry. For the present experiments, the thickness errors are estimated to be below 20 %. A description of the UHV chamber can be found in reference [9].

The optical measurements were performed with a differential reflectivity technique, to be discussed elsewhere, which is similar to the techniques used by other authors [10, 11]. The principle of the experimental method is the following : a monochromatic optical beam is focussed on an oscillating (800 Hz) mirror which alternatively directs it on the two halves of a sample : one of them is the clean « flat » surface and the other the same surface but covered with a silver overlayer. Use of a lock-in amplifier for the detection and feed-back control of the photomultiplier

Fig. 1. — Results of differential reflectivity measurements at normal incidence $\Delta R/\bar{R}$ vs. $\hbar\omega$, for different thickness d of the layers. — $d = 19 \text{ \AA}$; - - - $d = 124 \text{ \AA}$; - · - $d = 187 \text{ \AA}$; · · · $d = 2000 \text{ \AA}$. The last curve is reduced by a factor of 3.

high-voltage to keep a constant average level for the current, leads to $\Delta R/R = 2(R - R_0)/(R + R_0)$, R_0 and R being the reflectivities of the clean and perturbed surface respectively. A sensitivity of $\Delta R/R \sim 3 \times 10^{-4}$ in the 1.5-5 eV spectral range is obtained. Absolute values of $\Delta R/R$ are obtained after calibration of the spectra by measuring the absolute reflectivity of Ag deposits giving a substantial modification of the reflectivity ($\geq 10\%$). Reflectivity measurements were performed with a spectrophotometer similar to the one already described [9].

2. Results. — Clean smooth silver films about 0.1 μm thick are prepared by room temperature evaporation. They have a fibre structure consisting of microcrystals with the $\{1, 1, 1\}$ direction oriented perpendicular to the fused silica substrate and a smooth free surface. The smooth silver film is then cooled to 140 K (the temperature being measured at the silica-vacuum side of the substrate) and half of its area is covered with increasing amounts of silver which are deposited at a rate of about 40 $\text{\AA}/\text{min}$. in order to obtain surfaces with variable roughness. Figure 1 shows the measured values of $\Delta R/R$ vs. the incident photon energy for nearly normal incidence and for several Ag layers of increasing thickness. In order to understand the real significance of the curves, one should remember that the reflectivity of a thick silver film reaches very small values in the vicinity of the plasma frequency ($\hbar\omega = 3.79$ eV). The two sharp peaks with opposite signs in

Fig. 2. — Computed results of differential reflectivity. The thickness of the overlayer is 57 $\text{\AA}$. The relaxation time of conduction electrons is reduced by a factor of 2, and the interband contribution to the dielectric function is shifted of 50 $\text{\AA}$ towards large wavelengths. — : without roughness; - - : with roughness; the root-mean-square deviation is $S = 30$ $\text{\AA}$, and the width of the Gaussian correlation function is $\sigma = 300$ $\text{\AA}$; - . - . : $S = 30$ $\text{\AA}$ and $\sigma = 1000$ $\text{\AA}$.

$\Delta R/R$ are due to slight modifications of the Ag optical constants in the overlayers with respect to substrate film, the effects of which are greatly enhanced because of the small values of R .

To describe roughness we have used a second order approximation theory given by Kretschmann and Kröger [12], which assumes statistical roughness with a rms deviation S of the surface from perfect flatness and a Gaussian transverse correlation function $G(\mathbf{r}) = \exp(-r^2/\sigma^2)$. Silver deposits on cold substrates have a poor crystallographic structure and their optical constants differ from those of bulk Ag. To take this into account, we have modeled the surface deposit by a thin layer with thickness corresponding to the mean value of the deposited amount of silver and a reflexion coefficient at the Ag/vacuum interface given by equation (20) from Kretschmann and Kröger's work [12]. It is known that the Ag layers quench-evaporated on a cold substrate have a much smaller relaxation time than well-annealed films, the interband transitions being also modified. The positive peak at about 3.9 eV in figure 1 is indicative of a small shift of the absorption edge. For the Ag substrate we have taken the optical constants from reference [13] and for the surface layer we have assumed a free-electron relaxation time having half the value determined by Dujardin and Thèye [13]. This figure was estimated from the modification reported by Nguyen Van *et al.* [14] of the d.c. resistance of quenched films during annealing. In a rather arbitrary way, we have shifted by 50 Å towards the long wavelengths, the contribution of the interband transitions to the dielectric constant. The main effect is to shift the absorption edge in agreement with reported experiments [15]. Although the intensity and the shape of

Fig. 3. — Results of differential reflectivity measurements at normal incidence $\Delta R/\bar{R}$ vs. $\hbar\omega$, for a 158 Å thick layer, during the annealing at different temperatures of the sample. ···· : $T = 145$ K; ---- : $T = 193$ K; — — : $T = 230$ K; — : $T = 260$ K.

the peaks around 3.9 eV are strongly dependent on the dielectric constants, their exact values are irrelevant for the ideas discussed here.

Figure 2 shows the computed values of $\Delta R/R$ at normal incidence with $d = 57 \text{ \AA}$, $S = 30 \text{ \AA}$ and correlation distances $\sigma = 300$ and $1\,000 \text{ \AA}$ as well as for a flat smooth surface (continuous line). In figure 2 the low energy minima correspond to surface plasmon absorption, indicating that the main effect seen in figure 1 in the vicinity of $\hbar\omega = 3.6 \text{ eV}$ for the thinner layers is due to this effect. The computed curve for $\sigma = 300 \text{ \AA}$ is quite similar to the experimental data for the $57 \text{ \AA}$ thick layer. This value is indeed approximately the periodicity of the roughness of this film as observed by electron microscopy at room temperature by a method which will be described elsewhere, based on the « quenching » of the surface roughness by a very thin Al oxide layer.

A small absorption peak at about 2.5 eV is visible for the thinner layers; for increasing layer thickness, this absorption is also increasing but is hidden by the strong surface-plasmon excitation. In the experiments with definitely thicker films, this « anomalous » absorption became more and more conspicuous with increasing thickness and finally it could be clearly observed as in the experiments already mentioned [1]. The dotted curve in figure 1 corresponds to a $2\,000 \text{ \AA}$ thick deposit evaporated on a thick silver film. We should like to point out the difference between the experiments on cooled amorphous substrates as reported in references [5, 6] and the experiments presented here. The Ag overlayers investigated by us were deposited on clean crystalline metal substrates, which induces homoepitaxial growth. The situation is then different from that occurring when Ag is condensed on glass or air-oxidized metal substrates, which leads to nucleation

Fig. 4. — Intensity of the differential reflectivity signal during annealing. — : $\lambda = 3\,510 \text{ \AA}$ (maximum of the surface plasmon absorption); — : $\lambda = 5\,145 \text{ \AA}$ (wavelength of the laser source used in Pockrand and Otto's experiments); - - - is the intensity of the pyridine peak at $1\,006 \text{ cm}^{-1}$ measured by Pockrand and Otto [16], during the annealing of the silver substrate.

growth. This results in deposits consisting of small crystallites separated by grain boundaries and having a large amount of bulk defects and also large surface roughness.

Figure 3 shows the effects of annealing at a rate of ~ 1 K/min. on $\Delta R/R$ for a silver film 158 Å thick deposited on Ag. It is clear that the absorption peak centred at about 3.5 eV disappears with increasing temperature. This effect must be attributed to changes of surface topology only.

Figure 4 shows the $\Delta R/R$ variations as a function of temperature at two wavelengths $\lambda = 3\,510$ Å ($\hbar\omega = 3.53$ eV) and $\lambda = 5\,145$ Å ($\hbar\omega = 2.41$ eV), the latter value corresponding to the excitation wavelength used by Pockrand and Otto [16] for their SERS experiments. The SERS of pyridine for the $1\,006\text{ cm}^{-1}$ mode taken from reference [16] is also represented as a discontinuous line. The maximum of the SERS signal corresponds to the temperature region where $\Delta R/R$ is rapidly decreasing. The relationship between both curves is not clear to us, but the $\Delta R/R$ vs. T variation can be understood as a continuous decrease of the root-mean-square roughness height. The shape difference between the $\Delta R/R$ and SERS intensity curves vs. temperature suggests that classical enhancement related to high electromagnetic fields at the surface due to surface plasmon excitation is not the main contribution to SERS. As for a possible influence of localized modes related to surface plasmons at geometrical surface structures (e.g. bumps, pits) our experiments do not provide enough information. This point is now under investigation.

Acknowledgments. — We thank Professor A. Otto and Dr. A. Wirgin for useful discussions.

We wish also to thank Professor F. Abelès for his constant interest in our work and for his advice and suggestion while preparing this paper.

The research reported herein has been sponsored in part by the United States Army through its European Research Office.

References

- [1] HUNDERI, O. and MYERS, H. P., *J. Phys. F* **3** (1973) 683.
- [2] NGUYEN VAN, V., Private communication.
- [3] HUNDERI, O., *Phys. Rev. B* **7** (1973) 3419.
- [4] DITELLA, D. P., LIPSON, R. M., MCBREEN, P. and MOSKOVITS, M., *J. Vac. Sci. Technol.* **18** (1981) 453.
- [5] MOSKOVITS, M. and DITELLA, D. P., *Surface Enhanced Raman Scattering*, ed. by R. K. Chang and T. E. Furtak (Plenum Press, New York) 1982, p. 243.
- [6] OTTO, A., POCKRAND, J., BILLMANN, J. and PETTENKOFER, C., in reference [5], p. 147.
- [7] WOOD, T. M., *Phys. Rev. B* **24** (1981) 2289.
- [8] OTTO, A., to be published.
- [9] LOPEZ-RIOS, T. and VUYE, G., *J. Phys. E* **15** (1982) 456.
- [10] BEAGLEHOLE, D. and ERLBACH, E., *Phys. Rev. B* **6** (1972) 1209.
- [11] NASTASI-ANDREWS, R. J. and HUMMEL, R. E., *Phys. Rev. B* **16** (1977) 4314.
- [12] KRETSCHMANN, E. and KRÖGER, E., *J. Opt. Soc. Am.* **65** (1975) 150.
- [13] DUJARDIN, M. M. and THÈYE, M. L., *J. Phys. Chem. Solids* **32** (1971) 2033.
- [14] NGUYEN VAN, V., GANDAIS, M. and COUZINEAU, M. M., *Congrès International sur les couches minces*, Cannes, France, October 1970, *Le Vide* **147** (1970) 107.
- [15] WINSEMIUS, P., Thesis Leiden University (1973).
- [16] POCKRAND, J. and OTTO, A., *Solid State Commun.* **38** (1981) 1159.