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SURFACE PLASMON OF Ag CLUSTERS ON ALUMINA FILMS*

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The deposition of silver on an ordered alumina film prepared on Re(0001) surface has been studied by Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and high resolution electron energy loss spectroscopy (HREELS). The results show that Ag grows initially as clusters at 90K and 300K. A red shift of the Ag surface plasmon as a function of decreasing coverage is observed, which is related to the cluster size effect. A surface plasmon characteristic of metallic Ag appears at coverages higher than 2.8 monolayer equivalent.

Keywords: surface plasmon, nano-scale Ag clusters, particle size effect
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Nano-scale metal clusters between 1 and 10 nanometers in size exhibit physical and chemical properties differing from the bulk materials that vary as a function of cluster size. The geometric and electronic properties of clusters have been studied with various techniques including electron or optical spectroscopies.[1−5] Recently, high resolution electron energy loss spectroscopy (HREELS) has been used to measure the plasmon excitation of Silver.[6] The surface plasmon of silver as a function of cluster size has received considerable theoretical and experimental attention because of the important role silver plays as a technical catalyst.[6−10] The size-dependent surface-plasmon resonance of silver particles in various matrices has been studied including bare silver clusters;[8−11] however, no studies have involved the surface plasmon of silver clusters on an oxide substrate. We have recently developed a method for synthesizing ultrathin oxide films on refractory metal substrates that facilitates the use of various surface analytical methodologies, especially the electron or ion spectroscopies, as the result of elimination of the sample charging problem for insulating surfaces.[12]

In this paper, we will give some results to show that Ag initially grows on an ordered alumina film as clusters. The goal of this work is to have a more comprehensive understanding of the growth morphology of Ag on alumina as well as the change in the surface plasmon excitation as a function of cluster size at different substrate temperature. The experiments were carried out in an UHV chamber with a base pressure 2×10^{-10} Torr. The chamber was equipped with reverse view optics for low energy electron diffraction (LEED), electron optics with single-pass cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES), and an LK-2000 model spectrometer for HREELS. Al_2O_3 films were prepared by depositing Al onto the Re(0001) surface in ambient O_2 as described previously.[13] Ag was deposited using a high purity Ag wire wrapped tightly around a tantalum filament, which was thoroughly degassed prior to deposition. The rate of deposition of Ag was calibrated to be 27 minutes per monolayer. Since Ag is not necessarily grown on alumina film layer-by-layer, we prefer to use the monolayer equivalent (MLE) as a measure for Ag coverage. After each experiment, the surface was cleaned by annealing to 1200K prior to any subsequent experiments. The sample can be either heated at the desired temperature using an electron beam heater located at the back side of the sample or cooled down to 90K using liquid nitrogen. A W-5%Re/W-26%Re thermocouple was spot welded to the edge of the sample for temperature measurements.

The Al_2O_3 film prepared prior to the deposition of the Ag was characterized by LEED, AES and HREELS. LEED showed a diffuse hexagonal pattern with 1×1 surface structure while AES yielded a spectrum characteristic of Al_2O_3. HREELS data exhibited a surface phonon spectrum essentially identical to that reported previously.[13]

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The growth of Ag on the Al_2O_3 film was carried out at 90 and 300 K respectively. The AES spectrum of the 0.06 MLE Ag coverage on the alumina film at 300K is presented in Fig.1(a) along with the spectrum from the clean alumina substrate. Figure 1(b) is the HREEL spectrum. From the clean alumina film, the main loss peak at ca. 8.4eV is lower in energy than the band gap of bulk Al_2O_3, ~9.5eV. This surface therefore exhibits a spectroscopic window from ~2eV to ~6.5eV which facilitates the study of overlayer electronic structure such as the surface plasmon of Ag. The loss feature associated with the surface plasmon of Ag is apparent in Fig.1(b) at 3.52eV. The primary beam energy of 25 eV assures that the loss observed in Fig.1(b) corresponds primarily to the surface plasmon, that is, there is little contribution in this feature from the bulk plasmon.

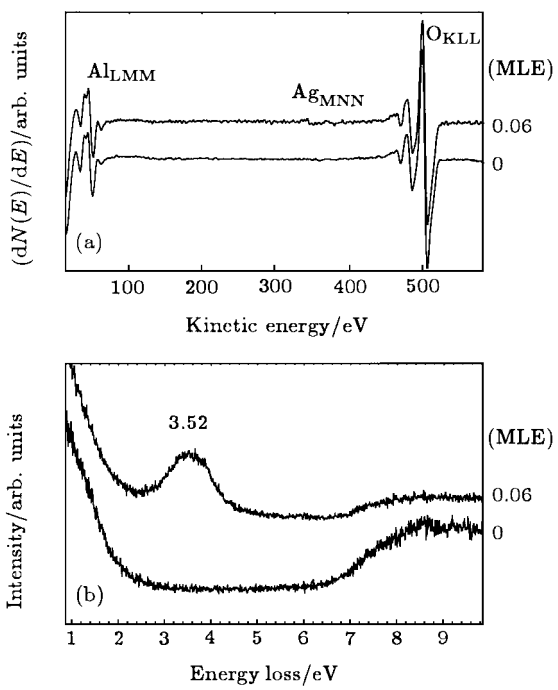


Fig.1. (a) AES of a clean Al_2O_3/Re(0001) substrate and a 0.06 MLE Ag deposited on it at RT, E_p=3keV. The kinetic energy of Ag_{MNN} electron transition should be 351 and 358eV. (b) EEL spectra of a clean alumina film and 0.06 MLE Ag/Al_2O_3/Re(0001) at RT, E_p=25eV, θ_i=θ_s=60°.

Studies of the surface plasmons of Ag and Ag deposited on different matrices have been addressed by both theorists and experimentalists.[6,14–28] HREEL data show that the electron energy loss of a surface plasmon depends on the momentum transfer parallel to the surface, determined by the incident and scattering angles, the primary beam energy and the loss energy of the surface plasmon as follows:

$$q_{\parallel} = \frac{\sqrt{2mE_i}}{\hbar}(\sin\theta_i - \sqrt{E_l/E_i}\sin\theta_s),$$

where $q_{\parallel}$ is wavevector transfer; m is the electron mass, E_i is the incident energy; E_l is the electron energy loss; θ_i is the incident angle, θ_s is the scattering angle. The surface plasmon from a Ag(001) single crystal is found at 3.79 eV;[7] from a Ag(111) clean surface the corresponding loss has been reported at 3.7 to 3.9 eV.[29]

The loss energy from 0.06 MLE Ag deposited on the alumina film is ca. 0.2 to 0.4 eV lower than that from metallic Ag, consistent with the fact that clusters formed at this Ag coverage have properties distinctly different from those of the bulk Ag. The size of Ag clusters formed on the same surface, namely the alumina film prepared on the Re(0001) surface, has been studied by scattering tunneling microscopy (STM).[30] At coverage of 0.05 MLE, Ag clusters have various sizes of 1–3nm in diameter, suggesting the beginning of three-dimensional (3D) growth of clusters.

The HREELS of the surface plasmon as a function of Ag coverage are shown in Fig.2. The loss energy of the surface plasmon gradually changed from 3.52 to 3.91eV with increasing coverage from 0.06 to 3.8 MLE. The peak at ~8.5eV from substrate gradually attenuated with increasing Ag coverage (not shown). At the coverage >2.8 MLE, the surface plasmon was independent of further increase in Ag coverage and exhibits a loss feature characteristic of metallic Ag.

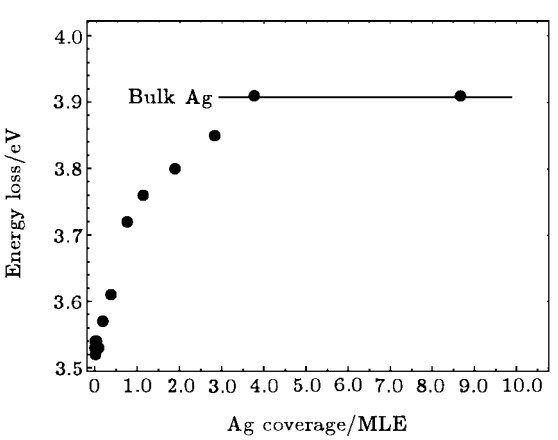


Fig.2. The energy shifts of Ag surface plasmon as a function of coverage at 300K, E_p=25eV, θ_i = θ_s=60°.

The data of Fig.2 show a shift of surface plasmon to lower energy with decreasing Ag coverage. The di-

rection of the shift in energy of the Ag surface plasmon (blue or red shift) with decreasing cluster size has been debated in the literature.[11,31–34] For example, using optical probes to study Ag clusters supported in matrices, i.e. Ag/CO or Ag/Ar colloids,[31] and Ag clusters embedded in Ar, Kr and Xe,[34] a blue shift was observed with decreasing cluster size. On the other hand, additional studies, e.g. with bare silver-particle aerosols,[11] showed a red shift with decreasing particle size. The surface plasmon frequency is strongly dependent on the valence electron density. The spillover of electron density from the metal clusters with limited dimensions then can lead to static polarizabilities well beyond the classical value, resulting in a shift of the surface plasmon to longer wavelengths, i.e. a red shift.[35] The results of this study agree well with published data for bare silver particles in which the surface plasmon energy is observed to shift from 3.8 to 3.4 eV as the average particle diameter is decreased.[11]

It is generally true that particle size increases with increase of coverage and ultimately the cluster's characteristics coincide with those of the bulk metal. This is reflected in Fig.2, in which the loss features are invariant beyond a coverage of 2.8 MLE. A detailed study of STM indicates that with the coverage increasing to 0.50 MLE, Ag clusters ranging from 3.0 to 7.0 nm in diameter were observed, Ag clusters coalesce and clearly evolve 3D hemispherical shapes with a low cluster density. Further increasing Ag coverage to 2.0 MLE, hemispherical Ag clusters increase to 6–10 nm in diameter and 2–5nm in height, while clusters smaller than 5.0 nm can also be seen.[30]

Different substrate temperatures during Ag deposition can result in a different cluster size distribution due to the migration of the atoms on the solid surface. The effect of deposition temperature on the loss energies is shown in Fig.3 at deposition temperatures of 90 and 300K. At 0.19 MLE coverage the plasmon loss peak is observed at 3.57eV at 90K and is found at 3.72eV at 300K (see Fig.3). It has been reported that cooling the Ag(111) sample causes an increase of the surface plasmon frequency without affecting the dispersion.[6] Our observation of a surface plasmon shift to lower energy at lower deposition temperatures along with result from Fig.2 suggests that any shift due to temperature and coverage decrease is offset by a particle size effect. Thus, the energy shifts show that the Ag clusters are smaller following decrease of coverage or deposition on a 90K surface than on a 300K surface.

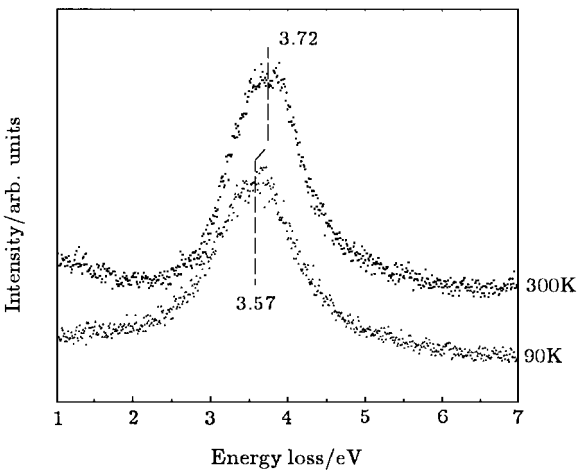


Fig.3. EEL spectra of $Ag/Al_2O_3/Re(0001)$ as prepared at 300K and 90K temperature with a coverage of 0.19 MLE, $\theta_i=\theta_s=60°$, $E_p=25eV$.

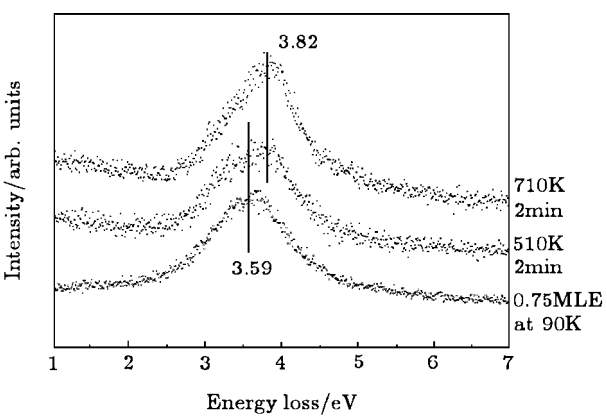


Fig.4. Energy shifts of the surface plasmon of Ag as a function of annealing temperature as indicated in the figures. Ag coverage is 0.75 MLE. $\theta_i=\theta_s=60°$, $E_p=25eV$, the data were received at 90K.

After heating the samples prepared at 90K temperature, the surface plasmon shifts towards higher energy as shown in Fig.4. The loss energy change from 3.59eV at 90K to 3.82eV at 710K for a coverage of 0.75 MLE sample demonstrates an increase in the cluster size after heating, i.e. the clusters become larger and, hence, more "bulk-like", which indicates that heating leads to the agglomeration of Ag, resulting in the exposure of more substrate surface. Recent studies of Ag on an alumina film and mica also demonstrated that annealing leads to "balling up" of Ag and to a partial freeing of the substrate surface.[36,37] Under 900K annealing for 2min, the surface plasmon of Ag clusters is rapidly reduced. Prolonged heating of the sample results in the disappearance of the surface plasmon.

Since the AES signal is not detected on this surface, it is most likely that the Ag is desorbed under this higher temperature treatment.

In conclusion, the energy shift of the surface plasmons of Ag deposited on alumina film on Re(0001) depending on the cluster "size" has been observed. Ag initially grows on the alumina film as clusters. The cluster size is relatively smaller at 90 K than that at RT. A red shifts of Ag surface plasmon with decrease of coverage is found. A characteristic of metallic Ag is found at coverage $\geq$2.8 MLE. After heating Ag deposited on the alumina film at 500K to 820K causes an agglomeration of Ag on the substrate.

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