Plasmon Confinement in Ultrathin Continuous Ag Films

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We investigate the effect of film thickness and granularity on the collective excitation of nanostructured ultrathin Ag films deposited on Si(111)7×7 by energy loss spectroscopy and low energy electron diffraction to obtain structural and spectroscopic information. For continuous thin films we find that the plasmon frequency at a vanishing wave vector scales with the surface-to-volume ratio of the grains, i.e., as the Mie resonance of separated clusters, instead of with inverse thickness. This indicates a confinement of the plasmon into single domains, in spite of metallic conductivity.

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Epitaxial growth of ultrathin metal films is at the center of the attention of surface physics and material science because of their role for manufacturing integrated circuits of increasing miniaturization. Ultrathin metallic films on semiconductors are of particular importance as they are the ultimate building blocks for nanosized integrated circuits. Additionally they provide the best model systems to study electrical transport phenomena in two dimensions, the conductance of the substrate being negligible at least at low crystal temperature.

Ag films on Si(111)7×7 can be grown epitaxially with excellent quality as demonstrated by the atomic flatness [1–3], the layer by layer growth mode [4], and by the onset of conductivity already at submonolayer coverage [5]. The percolation path of the film was readily observed by scanning tunneling microscopy (STM) [1,3]. For films deposited at a crystal temperature of $T = 100$ K, the conductance is well described by a simple Drude model with a mean free path given by the film thickness [5], while for room temperature deposition percolation is inhibited and conductivity is negligible.

Further information on the transport properties of such nanostructured films can be obtained from the electronic excitation spectrum and, in particular, from the collective modes. The understanding of the behavior of surface plasmons has greatly improved over the last years from both experimental and theoretical sides [6,7]. From the experimental point of view the application of energy loss spectroscopy low energy electron diffraction (ELS-LEED) has greatly improved the quality of the data by strongly increasing the resolution in reciprocal space [8] so that the investigation of more complicated systems is now possible. Silver was taken as a paradigm for the understanding of the effect of the presence of d electrons on the collective excitations [6]. Previous optical experiments showed that the frequency of the plasmon of a thin Ag film increases linearly with the inverse of the layer thickness [9], while for nanosized clusters the Mie resonance frequency increases with the inverse of the cluster radius [10]. Both dependences are determined by the same physical effect, i.e., the reduction of the surface to volume ratio [7].

Moreover, the interest for surface plasmons is motivated by the information obtainable from the coupling of plasmons with electromagnetic radiation, which is at the basis of several techniques such as the surface plasmon resonance [11] and the scanning plasmon optical microscopy [12]. Surface plasmons can be exploited in biosensing [11,13], gas sensing, characterization of thin films [14], and electrodeposition [15].

The experiment has been performed in ultrahigh vacuum (UHV) at a pressure of 2×10^{-10} mbar on a Si(111) single crystal. The sample was prepared in UHV by heating at 1200 °C to remove the oxide protecting layer and was then slowly cooled down to room temperature. The system was characterized by ELS-LEED, a technique which allows one to have access to both structural and spectroscopic information [15]. The structure of the Si surface was characterized by spot profile analysis of low energy electron diffraction (SPA-LEED), showing the characteristic diffraction pattern of the reconstructed Si(111)7×7 structure.

Ag was evaporated from a graphite crucible, heated by electron bombardment, while the crystal was kept either at room temperature or at 100 K. The amount of evaporated Ag was controlled with a quartz crystal microbalance, calibrated with Auger electron spectroscopy (AES), from the ratio of the Ag transition at 352 eV and of the Si transition at 92 eV. The structure of the polycrystalline Ag overlayer was characterized by SPA-LEED [16] and the lateral dimension of the Ag grains was evaluated from the full width at half maximum (FWHM) of the Ag $(1, 0)$ LEED spot. The thickness of the Ag layer was calculated considering that 1 monolayer (ML) of Ag corresponds to a thickness of 2.36 Å. The energy loss spectra were recorded with ELS-LEED [17], a spectrometer allowing for both high momentum and high energy resolution, at a crystal temperature of 100 K. For the present experiment the momentum resolution was 0.04 Å^{-1} and was limited

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by the quality of the Ag overlayer, while the energy resolution was tuned to 30 meV to improve the signal to noise ratio of the losses.

In Fig. 1 we present sample spectra recorded for different deposition temperatures and coverages at vanishing wave vector, i.e., for $q_{\parallel} = 0$. Similar data were recorded at other electron impact energies obtaining comparable results. The spectra present a single peak at a frequency close to the one of the Ag surface plasmon and can therefore be assigned to the collective mode of the overlayer. The position of the maxima was determined by a Gaussian fit to the peaks, while the momentum transfer was calculated by applying momentum and energy conservation. As one can see in Fig. 1A the plasmon frequency depends on layer thickness and, as it clearly appears in Fig. 1B, also from deposition temperature. The former dependence was forecasted by theory [7] and confirmed by an optical investigation of Ag/Si(111)7 $\times$ 7 [9]. The latter was never reported and must be connected to the nanostructure of the film.

For thin films, a linear dependence of the plasmon frequency at $q_{\parallel} = 0$ with the inverse of layer thickness t is expected [7]. The data are therefore collected in Fig. 2 vs $1/t$. As one can see, the data recorded for each deposition temperature T_{dep} follow such behavior closely. The slope of the linear dependence changes, however, with T_{dep} contrary to the expectation for a uniform thin film. The data for low T_{dep} coincide with the optical data of Borensztein *et al.* which were recorded in nearly identical conditions [9]. The triangles indicate data points corresponding to low T_{dep} followed by annealing to different temperatures.

The different $1/t$ dependence indicates that also the granularity of the film strongly influences the plasmon frequency of the overlayer. This parameter can be taken into account by a model for which the grains are considered as independent clusters. For the plasmon of Ag clusters (Mie resonance), theory [18] predicts a blueshift of the frequency with surface to volume ratio which scales as the inverse of the radius for spherical clusters, in accord with experiment [10]. The effect is related to the smaller influence of the d electrons on the oscillating charge located in the spill out region of the electron density. As the d electrons cause a redshift of the plasmon from its free electron value of 6.4 eV to the actual one of 3.7 eV, a reduction of their influence implies a blueshift which will scale with the variation of the surface to volume ratio with increasing cluster radius. The blueshift with the inverse of the film thickness bears the same origin.

For the Ag film deposited on Si(111)7 $\times$ 7 the domains nucleate inside both halves of the 7 $\times$ 7 unit cells and they grow layer by layer with vertical grain boundaries [1]. In accord with this observation we find that the average grain size area for deposition at 100 K coincides with the one of half a 7 $\times$ 7 unit cell. The grains are (111) oriented and show rotational disorder. The layer is flat, as a roughness smaller than 10% of the Ag lattice spacing is observed by SPA-LEED [16]. This result is in agreement with the very recent STM observation of the growth of flat Ag islands on Si(111) [3].

If we approximate the grains by cylinders, the surface to volume ratio is proportional to $1/x = 1/r + 1/t$, where r is the radius of the cylinder and t is its height. As demonstrated in Fig. 3 all data recorded in the dispersionless region of the spectrum fall, indeed, onto a single curve when plotted vs $1/x$. We notice that after this treatment also the data recorded for low temperature deposition and subsequently annealed at different temperatures and for different durations fall on the same line. As can be seen in Fig. 3, the dependence of plasmon energy with $1/x$ is approximately linear and a best fit yields 3.62 eV + 0.75/x eV.

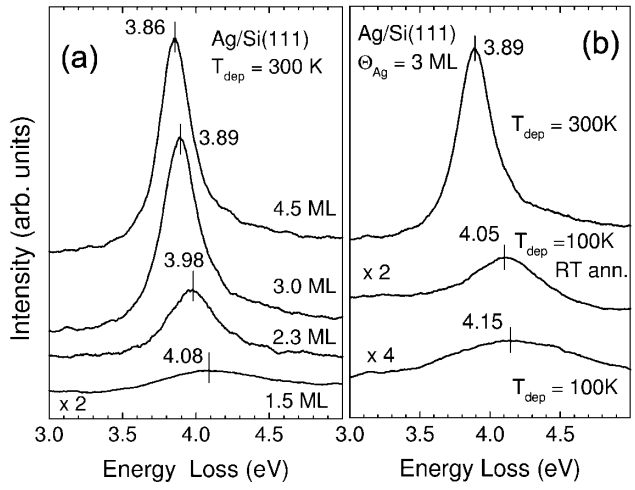

FIG. 1. Sample spectra recorded at $E_i = 56$ eV for (a) different layer thickness at $T_{\mathrm{dep}} = 300$ K and (b) different temperatures of deposition and annealing at 3 ML coverage.

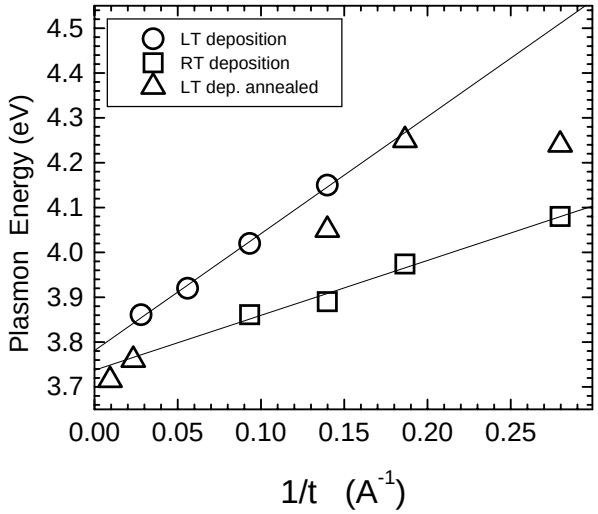

FIG. 2. Plasmon energy versus the inverse of the layer thickness. The continuous lines show the linear fit on the two sets of data collected for $T_{\mathrm{dep}} = 100$ K and $T_{\mathrm{dep}} = 300$ K.

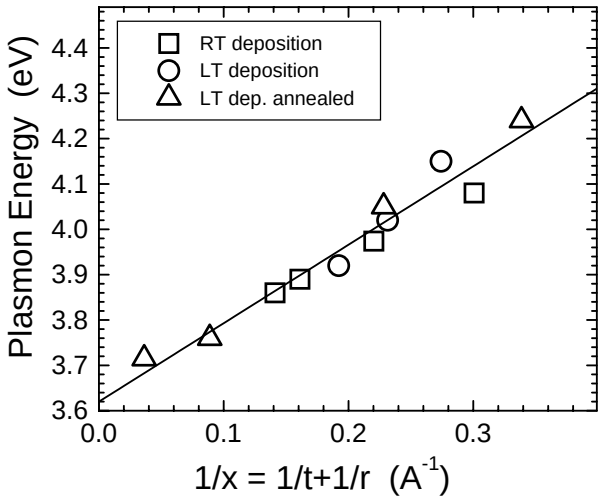

FIG. 3. Plasmon energy versus the surface to volume ratio of the grains. The continuous line is a linear best fit to the data. Two data points reported in Fig. 2 are not present here because the corresponding SPA-LEED data were missing and the determination of the average grain size was therefore not possible.

The $1/x$ dependence of plasmon frequency is indicative that the plasmons are confined into the single grains. Given this unexpected result, our experiment is a nice confirmation of existing theory [7] which predicts that the same physical mechanism is at the basis of the dispersion with $q_{\parallel}$ of the surface plasmon, of the $1/t$ dependence of the overlayer plasmon on a thin film, and of the $1/r$ dependence of the Mie resonance of clusters. Our data extend the range of cluster size well beyond the one obtainable with cluster sources.

Further evidence for plasmon confinement comes from the $q_{\parallel}$ dependence of the plasmon frequency. As shown in Fig. 4 the losses are independent of $q_{\parallel}$ up to a critical wave vector $q_{\parallel c}$ which coincides with $2\pi/d$, with d average island size determined by spot profile analysis of the (01) LEED peak of the Ag overlayer. The corresponding values of $q_{\parallel c}$ are given in Fig. 4 by the vertical bars. The granularity of the film is thus reflected also in the dispersion of the collective excitation with $q_{\parallel}$. The absence of dispersion below $q_{\parallel c}$ indicates that the s electrons oscillate independently in the single grains and that no propagation takes place for modes with a wavelength smaller than the diameter of the grains.

In conclusion, our results show the following: (1) The granularity of the film affects its collective properties. (2) The collective mode appears to be confined within the single domains of the thin film; propagation can take place only for modes whose wavelength is smaller than the diameter of the single grains. (3) The grains behave like isolated clusters with respect to the collective excitation in spite of the metallic behavior.

In agreement with our data, STM investigations [2] confirm that the morphology of the room temperature deposited films consists of relatively large (several 7×7 unit cells), well separated, grains while the conductivity of the film is negligible.

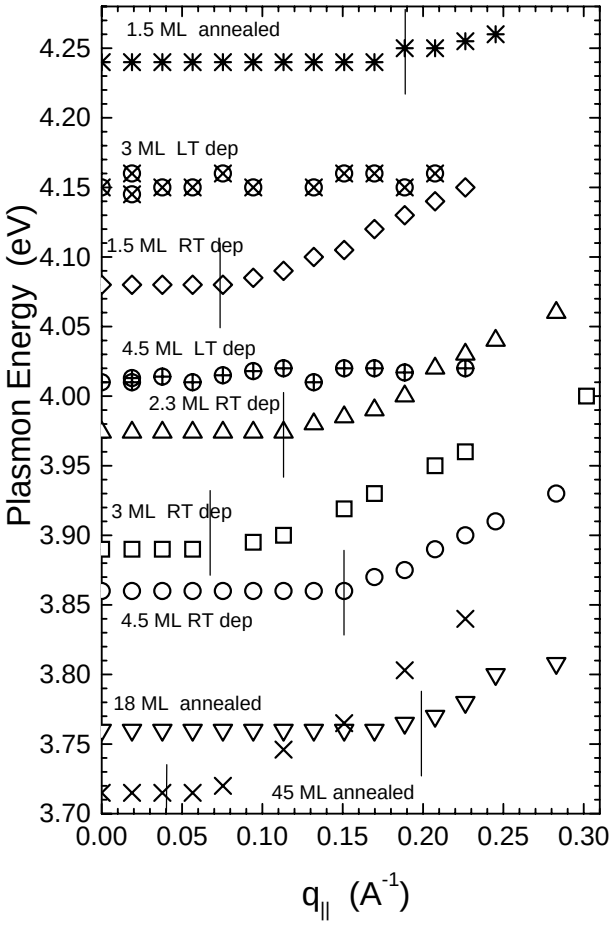

FIG. 4. Plasmon dispersion versus $q_{\parallel}$ for different Ag coverages for $T_{\mathrm{dep}} = 300$ K and for $T_{\mathrm{dep}} = 100$ K followed by annealing. The vertical lines indicate $q_{\parallel c} = 2\pi/d$.

At 90 K on the contrary, the STM images [1] and our SPA-LEED analysis indicates that the substrate is completely covered and that the grains are in contact. dc conductivity starts, indeed, at 0.7 monolayer coverage [5]. The grain size coincides with the 7×7 half unit mesh and does not increase with film thickness.

How can one reconcile a plasmon confinement with touching grains at 100 K?

One first guess could be that confinement occurs due to problems in coupling the band structure, since the grains are rotated against each other within about 6° [15]. On the other hand, dc conductivity is not at all affected by the grain boundaries [5] and localization occurs only for very small thickness (2 ML) and very low temperatures (less than 20 K). The high frequency of the plasmon should, moreover, bridge the gap and not open it.

We can imagine two alternative mechanisms leading to a plasmon localization. One model asks for a strong contribution of the d bands which are responsible for the shift of the plasmon frequency from its free electron value to its actual value [18]. At $q_{\parallel} = 0$ such shift is strongly

face dependent [8], because of the face dependence of the *d* band dispersion. We can expect that the *d* states will be quite different at the grain boundary as the average interatomic distance is increased by some 50% in that area. The plasmon could thus be unable to propagate over such a region, thus leading to localization in the single grains.

Alternatively one could take into account the observation that the grain boundaries dominate the morphology of film growth. STM pictures show that the film has monatomic islands in the size of the grain. Since the plasmon resonance depends on film thickness, neighboring grains might have different resonances which do not easily couple, again yielding localized modes.

Unfortunately theoretical model computations are not yet available. Experiments on nanostructured alkali metal films should enable one to distinguish between the two models; as for the latter the presence of *d* electrons plays no role.

In conclusion, we have demonstrated that the plasmon of ultrathin Ag films grown on Si(111) is confined within the grains in spite of the metallic behavior shown in conductivity experiments.

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