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Size-selected Ag_n and Cu_n clusters supported on MgO(100) films

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Abstract. Small Ag_n ($n \leq 13$) and Cu_n ($n \leq 7$) clusters, generated by sputtering with a new ultrahigh vacuum (UHV)-compatible Xe-ion gun and size-selected by a quadrupole mass spectrometer, are deposited *in situ* in submonolayer quantities on a magnesium oxide film supported on a molybdenum single crystal. At low substrate temperature ($T = 45$ K), the measured electron energy loss spectra display characteristic losses within the MgO band gap. These novel results are discussed in terms of electronic transitions and plasmon excitations within the cluster.

PACS. 36.40.+d Atomic and molecular clusters – 79.20.Hx Electron impact: secondary emission

1 Introduction

For recent emerging fields in surface science, such as thin film growth and size-selected cluster deposition, oxides have played an important role in the study of surface-related phenomena, e.g., heterogeneous catalysis, diffusion, and epitaxial growth [1–3]. Preparation procedures and characterization of thin oxide films grown on various supports have been studied intensively during the last decade in an attempt to overcome the problem of sample charging, which occurs when spectroscopic techniques are employed. In addition, for scanning tunnelling techniques, thin insulating films will permit the probe current to tunnel to the metallic support [4, 5]. Particularly thin MgO(100) films have attracted much interest because of their structural and electronic properties [4–8]. Mass-selected clusters are known to display properties that are a function of their size [9–11]. Earlier experiments involving vapor-deposited Ag [12, 13] and Cu [14, 15] atoms have been performed on both MgO single crystals [12–14] and thin films [15]. Recently, we have investigated these two systems at low temperature with different spectroscopic techniques [16, 17] at a much higher energy resolution than in the former studies. For Ag on MgO, the growth mode (Volmer–Weber) at room temperature and the sticking probability between 100 K and 500 K have been previously determined [16]. Energy loss peaks have been identified as silver plasmons, and a relevant experiment has permitted researchers to attribute one of them unambigously to the Ag–MgO interface plasmon [16]. For Cu on MgO, thermally evaporated atoms have been investigated as a function of coverage and substrate temperature, and a diffusion energy $E_\mathrm{d} = 0.50 \pm 0.05$ eV has been determined [17] that is in good agreement with theoretical predictions [18]. In this work, we show a spectroscopic electron energy loss (EELS) study of size-selected Ag_n ($n \leq 13$) and Cu_n ($n \leq 7$) clusters supported on an MgO(100) film.

2 Experimental

The experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure of 2×10^{-10} mbar, which allowed *in situ* characterization of the sample by low energy electron diffraction (LEED), electron energy loss spectroscopy (EELS, HREELS) [16, 17] and photoemission spectroscopy (UPS, XPS) [19–21] (Fig. 1). For EELS, monochromatized electrons of primary energy $E_\mathrm{p} = 30$ eV and beam current $I \approx 1$ nA were focused on the sample with an angle of 50° with respect to the surface normal of the sample. The EELS spectra were obtained under normal emission by the collection of secondary electrons using a hemispherical electron analyzer (HA 150 from VSW). The total instrumental energy resolution was set to 100 meV, and the angular resolution was ±2°. Ionized clusters were produced by Xe-ion bombardment of a metallic target [22] with a new UHV-compatible CORDIS ion source [19]. Subsequently they were mass-selected by a quadrupole mass spectrometer (Extrel Model 4-162-8) and deposited at different kinetic energies [20] on a thin 20 ± 2 monolayer (ML) MgO(100) film grown at room temperature on an Mo(100) single crystal [6, 7]. The quality and thickness characterizations of the MgO film are shown elsewhere [16]. Briefly, sharp LEED patterns, multiple phonon losses in the HREELS spectrum, and the characteristic UPS emission from the O 2*p* valence band indicate a well-ordered MgO(100) single crystal surface; this

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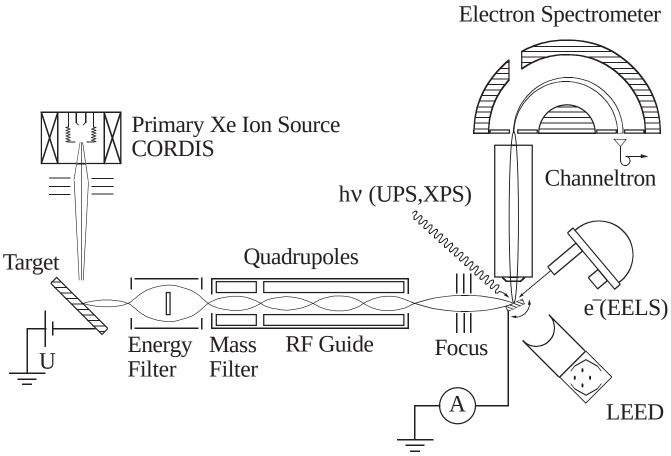

Fig. 1. Schematic view of the experimental setup for the production, size selection, deposition, and *in situ* characterization of the clusters with low-energy electron diffraction (LEED), electron energy loss (EELS, HREELS), and photoemission (UPS, XPS) spectroscopy. Coverage is monitored by the measurement of the cluster current on the sample.

is in good agreement with previous studies [6,7,23,24]. Auger electron spectroscopy (AES) measurements, which have been undertaken by our group on these MgO films, show their one-to-one stoichiometry and the absence of C impurities [25]. The substrate temperature measured directly on the sample with a spot-welded W-26%Re/W-5%Re thermocouple was maintained at $T = 45 \pm 5$ K with a liquid helium flow cryostat.

3 Results and discussion

Figure 2 displays EELS spectra taken at $T = 45$ K for 0.04 ML of Ag_n ($n \leq 13$) clusters deposited from the cluster source at the lowest possible kinetic energy ($E_\mathrm{k} = 3$–6 eV) to prevent their fragmentation [26]. Each deposition was made on a freshly prepared film to avoid the creation of defects that are known to act as pinning centers for deposited clusters [27,28]. We observed several distinct energy loss peaks appearing within the MgO band gap (between 1 eV and 5.5 eV energy loss [16]) as a function of cluster size. These loss peaks cannot be assigned to low-lying transitions in the atom or in the ion [29–32]. EELS spectra of vapor-deposited Ag, which forms islands and thin films via surface diffusion at sample temperatures between $T = 100$ K and 500 K, have shown losses at 3.8 eV and 3.2 eV that are attributable to the Ag surface plasmon and to the Ag–MgO interface plasmon, respectively [16]. In contrast, the present EELS spectra recorded at $T = 45$ K exhibit clearly a size dependence that reflects the change in the electronic structure of the clusters. A similar behavior has been observed in optical absorption spectra of Ag_n ($n \leq 21$) clusters deposited in rare gas matrices [33] and has been interpreted as a manifestation of collective excitations (Mie plasmons) of the *s* electrons influenced by the ellipsoidal shape of the clusters. Some similarities in the general trend can be observed between the optical absorption data shown in [33] and our EELS experiment. We note that EELS probes electronic excitations and transitions which are dipole forbidden ($\Delta l \neq 1$) in addition to those observed by absorption spectroscopy ($\Delta l = 1$). A shift towards lower energy loss ($\Delta E = 0.2$–0.3 eV) in our case may be due to a different environment, e.g., different dielectric constants: MgO versus rare gas). Furthermore, changes in the peak shapes may be attributed to the loss of central symmetry in our experiment (surface versus matrix) and/or to different cross sections of the emission process.

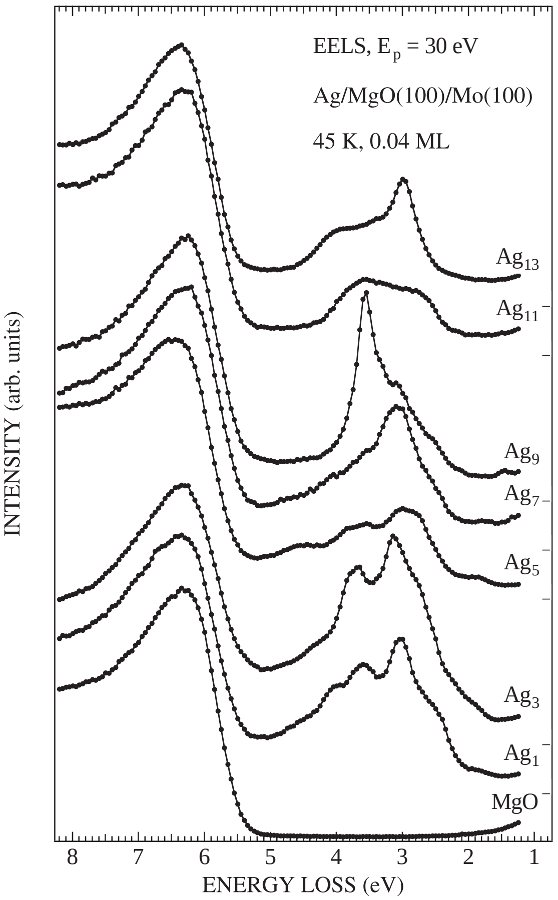

Fig. 2. EELS spectra of the bare MgO(100) film and 0.04 ML of size-selected Ag_n ($n \leq 13$) clusters deposited on the same film held at $T = 45$ K.

Figure 3 displays EELS spectra taken at $T = 45$ K for 0.04 ML of vapor-deposited Cu and Cu_n ($n \leq 7$) clusters deposited from the cluster source. The three characteristic energy loss structures observed for the atom are attributed to low-lying transitions in the Cu atom and Cu^+ ion, as discussed in [17]. However, it is still unclear why some atomic and ionic transitions in our EELS spectra are much more intense than others in a given multiplet. The adsorption site for Cu on the MgO(100) surface is predicted to be on top of an oxygen atom [18]. The poor statistics of the cluster data are due to the rapid decrease versus time in spectral intensity observed for all Cu deposits. Electron stimulated desorption (ESD) [34] has been excluded as an explanation because of an unusually high cross section of the

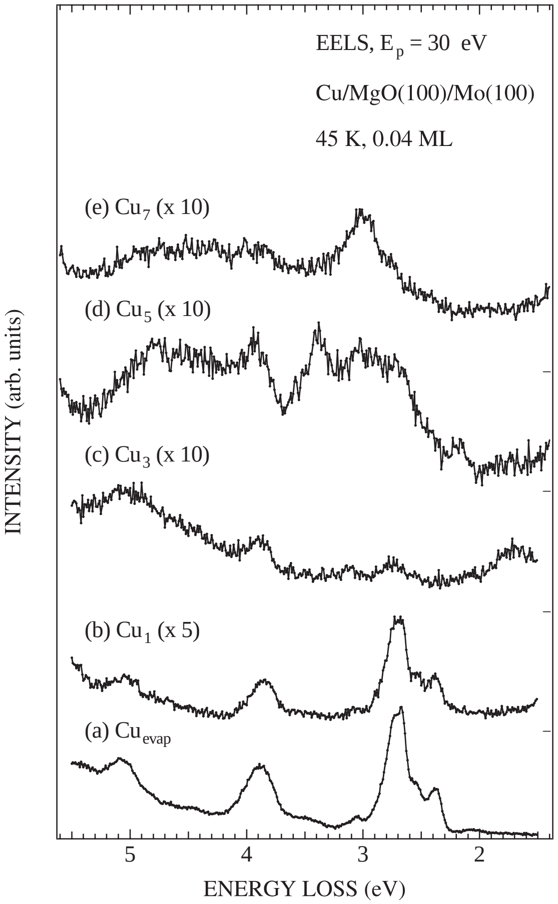

Fig. 3. EELS spectra of 0.04 ML of vapor-deposited Cu and size-selected Cu_n $(n \leq 7)$ clusters deposited on an MgO(100) film held at $T = 45$ K.

phenomenon. We propose a modification of the Cu–MgO interaction leading to Cu oxide formation (CuO or $\mathrm{Cu_2O}$). On the other hand, EELS data show a strong dependence upon oxygen adsorption that leads to a total extinction of the initial Cu signal, while a very weak and relatively broad energy loss structure at 2.2 eV and 4.2 eV emerges that can be related to emission observed from thin copper oxide films [35]. The positions and shapes of the three main losses in the cluster spectra are almost unchanged; this shows a strong similarity with the vapor deposition of Cu atoms [17]. For $\mathrm{Cu_3}$, two other energy loss peaks appear at 1.8 eV and 3.1 eV. For Cu dimers, we observe a similar spectrum (not shown). We note that these two additional losses for the Cu dimers and trimers are located at the same loss energy as that observed for the higher coverage case ($\theta > 0.12$ ML) of Cu atoms [17]. By taking into account the experimental value for the binding energy of Cu dimers ($E_{\mathrm{B}}(\mathrm{Cu_2}) \approx 2$ eV [36] as compared to the deposition energy $E_{\mathrm{k}} = 3$–6 eV per cluster), we conclude that most probably a fraction of the clusters undergo fragmentation on surface impact. In Table 1, we summarize the electronic transitions in free and matrix-isolated Cu_n clusters observed with optical absorption spectroscopy [37–39] those and of the present study. We note encouraging agreement between the results obtained by the two methods. However, we cannot exclude that charge transfer excitations from the cluster to the MgO substrate or vice versa are present in the spectra. We hope that in the future, additional experimental data, especially from scanning tunnelling microscopy, will give a better insight into the role of defects and into diffusion and island formation.

4 Summary

Atoms and size-selected Ag_n $(n \leq 13)$ and Cu_n $(n \leq 7)$ clusters were deposited at $T = 45$ K on a well-characterized MgO(100) film. EELS measurements revealed size-dependent energy losses within the MgO band gap that are assigned to plasmons and electronic transitions within the Ag and Cu clusters, respectively. A comparison with absorption experiments of Ag clusters in a matrix reveals similar structures. Energy differences between the two data sets are attributed to the different cluster environments.

Table 1. Comparison of optical absorption data of Cu atoms in the gas phase [37], Cu_n $(n \leq 3)$ clusters embedded in rare gas matrices (Ar [38], an Xe [39]), and our EELS observations. Peak positions are indicated in eV.

$\mathrm{Cu_{evap}}$		$\mathrm{Cu_1}$	$\mathrm{Cu_3}$		$\mathrm{Cu_5}$	$\mathrm{Cu_7}$
EELS	Absorption gas Ar Xe	EELS	EELS	Absorption Ar	EELS	EELS
			1.7			
2.4		2.4	2.4	2.5	2.2	
2.7		2.7	2.7			
						3
			3.2	3.3	3.4	
3.9	3.8 — 3.8	3.9	3.9		3.9	
	— 4.1 3.9					4
	— — 4.5			4.7	4.8	
5.1	5.1 5.2 5.0	5.1	5.1	5.3		5
	— 5.6 —			5.6		

For Cu clusters, in addition to size-dependent loss structures, we observe a similar spectroscopic fingerprint as for the isolated vapor- deposited Cu atoms; this points to partial fragmentation during the deposition process. These data are encouraging, for they demonstrate the feasability of detailed spectroscopic studies of size-selected clusters supported on oxide films.

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