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Electronic properties of metallic bilayers deposited on Cu(1 1 1): A comparative study

Antonio Politano [a,*], Vincenzo Formoso [a,b], Gennaro Chiarello [a,c]

[a] Dipartimento di Fisica, Università degli Studi della Calabria, Via Ponte Bucci, 2 Cubo 31/C, 87036 Rende (Cs), Italy
[b] Laboratorio regionale LICRYL, INFM-CNR, Università degli Studi della Calabria, 87036 Rende (Cs), Italy
[c] CNISM, Consorzio Nazionale Interuniversitario per le Scienze Fisiche della Materia, Università degli Studi della Calabria, 87036 Rende (Cs), Italy

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ABSTRACT

The nature and the dispersion of the electronic collective excitations in different metal bilayers (Na, Ca, Ag) deposited onto the Cu(1 1 1) surface were investigated by angle-resolved electron energy loss spectroscopy. We found a nearly-flat behavior of the surface plasmon energy (absence of dispersion) in Ca and Ag bilayers, characterized by the presence of d electrons, in good agreement with theoretical predictions within the framework of the s–d polarization model. On the contrary, an initial negative dispersion was observed in the Na bilayer. The intensity of the surface plasmon was vanishing in the long-wavelength limit in all cases.

1. Introduction

Collective electronic excitations in nanoscale systems have been widely studied in recent years [1–5]. In particular, the behavior of the surface plasmon (SP) dispersion in ultrathin films deposited on metal and semiconductor surfaces has been the subject of several theoretical [1] and experimental [4,6,7] investigations. Ultrathin films usually exhibit electronic properties markedly different from their bulk counterpart [8] as quantum size effects and electron quantum confinement may occur.

While semi-infinite media have been extensively investigated [2,9–12], experimental studies on low-dimensional systems, such as ultrathin films, nanowires or quantum dots are still lacking. On the other hand, it would be extremely useful to study dynamic screening processes in the case of metal bilayers deposited on metal substrates. In fact, two layers are commonly accepted as a borderline between interface physics and thin films physics [1,4,6,7]. As a matter of fact, such coverage constitutes the minimal thickness necessary to observe in the loss spectra well-distinct features assignable to collective excitations, while the very broad loss features observed from 0 to 2 ML are assigned to single-particle transitions [7]. In the case of simple metals it has been demonstrated that the nature of the collective electronic excitations in two layers [4,6,7] is very different from that of multilayers [13]. For alkali bilayers, the excitation of SP is forbidden at small momenta [1] and in this limit only bulk plasmon (BP) and multipole plasmon exist. Increasing the coverage above two layers, the excitation of SP becomes possible even in the long-wavelength limit (small $q_{||}$) [1].

Likewise, also for Ag films deposited onto metallic substrates the nature and dispersion of the collective excitations occurring in two layers have been predicted [1] to be different compared to the case of multilayers [5]. However, to the best of our knowledge, no experimental study supporting such theoretical findings [1] exists. Experiments carried out on ultrathin Ag films grown on Si(1 1 1) [14] reported a positive behavior of the SP dispersion and, moreover, the collective excitation observed at small momenta was assigned to the ordinary SP. These findings are in contrast with theoretical expectations within the framework of the s–d polarization model [1]. Hence, further experimental work aimed at investigating the nature of the collective excitations in metal/metal interfaces is needed. Such studies should provide a significant advancement in understanding dynamic screening processes in the limit of ultrathin metallic layers.

The general validity of the s–d polarization model could be efficiently probed by making a comparative study on bilayers of different metals grown on the same substrate.

Herein we present high-resolution electron energy loss spectroscopy (HREELS) measurements shedding light on the nature and the dispersion of the collective excitations in two layers of Na, Ca, and Ag on Cu(1 1 1).

* Corresponding author. Present address: Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad Autónoma de Madrid, and Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA), 28049 Madrid, Spain. Tel.: +39 984 496157; fax: +39 984 494401.
E-mail address: politano@fis.unical.it (A. Politano).

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The (1 1 1) surface of noble metals (Cu, Ag, Au) exhibits a large confined gap within the projected bulk band structure centered at the $\bar{\Gamma}$ point of the surface Brillouin zone [15]. Electronic states of different origin can exist in this gap. They may be Shockley surface states or states induced by adsorbates (quantum well states, QWS). In particular, photoemission spectroscopy measurements for Na and Ag films on Cu(1 1 1) demonstrated the existence of Na [16,17] and Ag [18–21] QWS of $3p_z$ and 5sp character within the adlayer, respectively. The presence of QWS has been revealed also for alkaline-earth thin films on Cu(1 1 1) [22]. This implies the occurrence of an enhanced sp density of states at the Fermi level that modifies the electron charge–density distribution, thus causing significant changes in the dynamical screening properties of these systems [23] with respect to the case of single-crystal surfaces. Hybridization between QWS and the substrate [24] may also influence the electronic response of the interface and it should be enhanced for reduced thicknesses, i.e. 2 ML.

Loss measurements reported here demonstrated that in metal bilayers the excitation of SP is not allowed at small momenta. Moreover, in adlayers characterized by the presence of d electrons (Ca and Ag) the SP energy exhibited a dispersionless behavior in agreement with the s–d polarization theory [1].

2. Experimental

HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The Cu(1 1 1) surface was cleaned by repeated cycles of ion sputtering and annealing at 950 K. Surface cleanliness and order were checked using Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) measurements, respectively. Sodium was deposited from a commercial getter source (Saes Getters, Italy). Calcium was evaporated by a heated tungsten basket containing Ca grains. Due to the higher reactivity of Na and Ca towards residual gases in the UHV chamber, each loss spectrum was acquired in few minutes in order to avoid contamination of the adlayer. Silver was deposited onto the Cu(1 1 1) surface by evaporating from an Ag wire wrapped on a tungsten filament. Coverages were calibrated using AES. The incident angle with respect to the sample normal was fixed at 55.0°. The energy resolution of the spectrometer was degraded to 10 meV so as to increase the signal-to-noise ratio for off-specular spectra. The measured angular acceptance α of our electron analyzer was ±0.5°. Dispersion of the collective mode, i.e. $E_{loss}(q_{||})$, was measured by moving the analyzer while keeping the sample and the monochromator in a fixed position. To measure plasmon dispersion, values for the parameters E_p, impinging energy, and θ_i, the incident angle, were chosen so as to obtain the highest signal-to-noise ratio. To obtain the energies of loss peaks, a polynomial background was subtracted from each spectrum. The resulting spectra were fitted by a Gaussian line shape (not shown herein).

All depositions and measurements were made at 300 K.

3. Results and discussion

3.1. Na bilayer on Cu(1 1 1)

Multilayers of alkali metals are easily grown on Cu(1 1 1) even at room temperature while in other systems the growth of a second alkali layer is possible only at liquid nitrogen temperature [25]. The occurrence of the $(3/2 \times 3/2)$ LEED pattern was used as the calibration point of $\theta_{Na} = 0.44$ ML.

Loss spectra in Fig. 1 shows the SP of two layers of Na/Cu(1 1 1) for different scattering angle. The SP energy is recorded 3.70 eV in the specular geometry and it exhibits clear dispersion for off-specular angles.

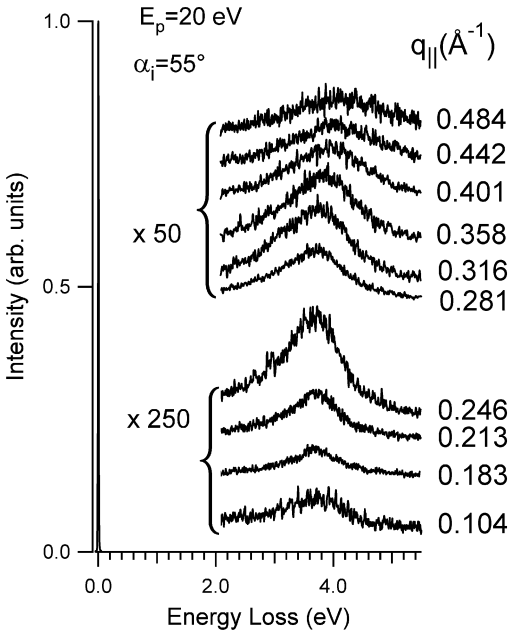

Fig. 1. Electron energy loss spectra of two layers of Na on Cu(1 1 1) at different scattering angles θ_s. The incident beam energy E_p was held constant at 20 eV and all spectra were recorded at an incident angle of $\theta_i = 55°$ with respect to the sample normal.

The measured dispersion curve $E_{loss}(q_{||})$ reported in Fig. 2 was fitted by a fourth-order polynomial [2] given by:

$$E_{loss}(q_{||}) = a + bq_{||} + cq_{||}^2 + dq_{||}^3 + eq_{||}^4$$

where $a = 3.99$ eV, $b = 0.70$ eV Å, $c = -29.53$ eV Å^2, $d = 113.14$ eV Å^3, and $e = -112.31$ eV Å^4.

The slope of the dispersion curve is negative up to 0.25 Å^{-1}, then the loss energy of the SP increases with increasing $q_{||}$ and the dispersion becomes definitively positive. Interestingly, the value of the parallel momentum transfer corresponding to the minimum of the dispersion curve is anomalous with respect to the common value found in others similar investigations, i.e. 0.15 Å^{-1} [7,12,26].

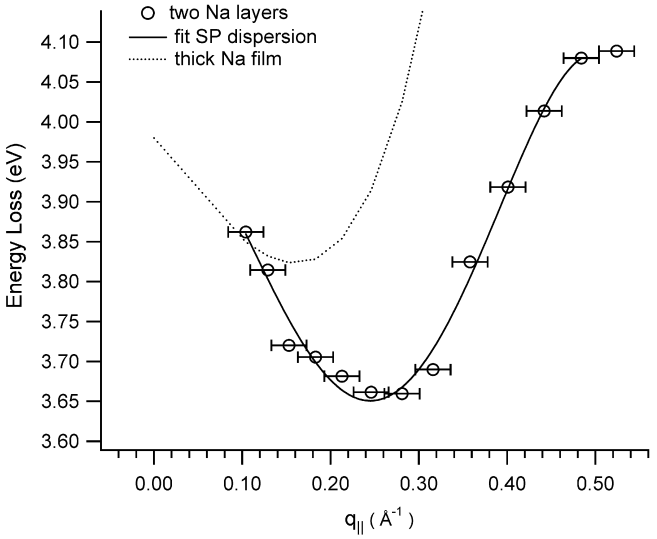

Fig. 2. The surface plasmon dispersion versus the parallel momentum $q_{||}$ for (○) two Na layers and (—) a thick Na film (data taken from Ref. [13]).