Epitaxy and Magnetic Properties of Surfactant-Mediated Growth of bcc Cobalt

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High resolution core level photoemission spectroscopy, photoelectron diffraction, and x-ray magnetic circular dicroism (XMCD) have been used to characterize the structural and magnetic properties of bcc-cobalt films grown on GaAs(110) substrates by using Sb as a surfactant. We have unambiguously disentangled the surfactant role played by the Sb which improves the crystallinity and reduces the lattice distortion of the metallic films as well as changes the interdiffusion process at the interface compared to the Co/GaAs(110) system. As a consequence of these combined effects, an improvement on the magnetic response of the grown Co thin films has been observed by XMCD measurements.

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The study of *ferromagnetic metal-semiconductor* interfaces has become one of the hot topics in surface science. In particular, the magnetic properties of the grown metallic films are very much distinct to those of the bulk materials due to the strain induced on their atomic structure [1]. Consequently, new magnetic phases not present in nature have been obtained, such as bcc cobalt on Fe/Ge(001) [2] or on GaAs [1,3–6].

Regarding the Co/GaAs interface, it has been shown that a distorted bcc-Co atomic structure can be grown on different faces up to a maximum thickness which depends on the lattice matching of the substrate surface and the grown film [1,7]. As the lattice parameter for the pure bcc cobalt is around 2.82 Å [1], almost perfectly half of the lattice parameter of GaAs ($a = 5.65$ Å), the growth of the bcc-cobalt films on the GaAs(110) surface is expected to proceed by accommodating two unit cells of the Co(110) to one of the substrate (see Fig. 1).

However, the growth of transition metals on semiconductors substrates is very complex and generally affected by a reaction at the interface, which strongly influences the magnetic properties [8,9]. In particular, for the Co/GaAs(110) system, a strong reaction has been previously reported [3,5], which leads to a reduction of the experimental magnetic moment with respect to the theoretical expectations for the bcc phase [10,11] and to the bulk hcp corresponding values [1]. This reduction has been theoretically explained in terms of poisoning by As diluted into the Co matrix [8] which would also be responsible for the existence of a magnetically dead interface of around 10–25 Å [12]. In this context, an improvement of the crystallinity and a reduction of the interface reaction has been experimentally intended by means of either seed [2,13] or passivating layers [5,14,15], which sometimes develop fcc or hcp phases [13,15]. Among the results maintaining the bcc phase, we have previously shown [5,16] that treating the GaAs(110) substrate with Sb prior to Co deposition improves the bcc atomic structure [5,16].

In this Letter, we present a combined study of the atomic structure, the interface reaction, and the magnetic properties of the bcc-Co films grown on GaAs(110) by using the Sb as surfactant during the metal deposition. To achieve this goal, we have used a combination of different synchrotron radiation-based techniques. High resolution core

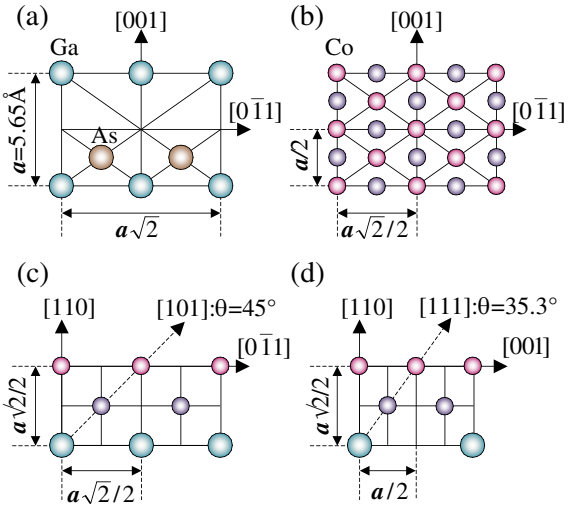

FIG. 1 (color online). Panels (a) and (b) show top view schemes of the atomic structure for the clean GaAs(110) substrate and the bcc-Co(110) surfaces. Lateral views of the Co/GaAs(110) interface along the high symmetry crystallographic directions [0$\bar{1}$1] and [001] are shown in panels (c) and (d).

level photoemission spectroscopy has put in evidence the surfactant role played by Sb and the magnitude of the interface reaction between the Co and the GaAs substrate. The atomic structure of the Co films has been determined by x-ray photoelectron diffraction (XPD). This surface sensitive technique has shown that the growth of Sb-mediated Co films results in a large improvement of the atomic structure. Finally, x-ray magnetic circular dicroism (XMCD) measurements have evidenced that, in contrast to previous observations [12], the Co/GaAs interface does not present a magnetic dead layer in the low coverage range. Moreover, a clear improvement on the magnetic properties of the Co thin films is induced by the Sb.

The experiments were carried out in ultrahigh vacuum conditions at the Super-Aco storage ring of synchrotron LURE in Orsay, France. The photoemission and photoelectron diffraction experiments were performed at the Spanish-French station connected to the SU6 and SU7 undulator beam lines, respectively, and the XMCD characterization was performed at the SU2 asymmetric wiggler of the SU23 beam line where the polarization rate of the obtained circular light was fixed to 70%. For more details related with the sample preparation and the experimental apparatus, we refer the readers to Refs. [5,16,17].

Figure 2 shows the evolution of the photoemission spectra of the Ga 3*d*, As 3*d*, and Sb 4*d* core levels as a function of the Co thickness in a range between 3 and 24 Å. The three photoemission peaks appear in a kinetic energy range between 34 and 56 eV where the electron escape depth varies between 3–4 Å, thus providing information from the outermost 10 Å of the interface. We can clearly observe that upon increasing the cobalt coverage on the 0.5 ML Sb/GaAs(110) surface the intensities of both the Ga 3*d* and As 3*d* peaks decrease and a drastic change in their lineshapes can be noticed. In contrast, the intensity of the Sb 4*d* remains constant with Co coverage. This means that antimony atoms are not buried by cobalt deposition but instead and, due to their low activated diffusion, they float on top of the Co layers. Moreover, the Sb core level lineshape only suffers one change after the first Co deposition and keeps constant during the subsequent metallic depositions. All these spectroscopic modifications appear as a result of the floating behavior of Sb atoms, which are able to slide along at the initial stage of the cobalt growth, clearly indicating the surfactant role of the Sb overlayer [18,19]. This result, which is interesting in itself, would be much more relevant if it could be related with a net improvement of the atomic structure and the magnetic properties of the cobalt films, as well as with a noticeable reduction of reactivity at the Co/GaAs interphase. This effect has already been reported in the case of S-passivation of the GaAs(110) surface prior to Fe overgrowth [20].

We have observed that antimony drastically modifies the interdiffusion process of the Ga atoms with respect to the nontreated surface. Figure 2(b) shows that the total intensity of the Ga 3*d* photoemission peak decreases as the Co coverage increases at a similar ratio to that of the As 3*d*

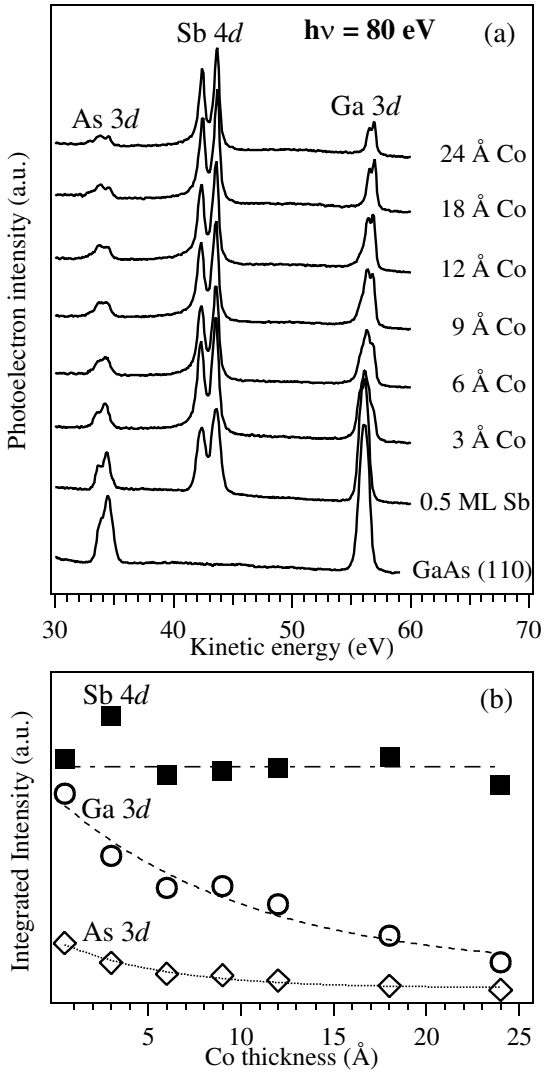

FIG. 2. Evolution of the photoemitted intensity (normalized to the photon flux) of the Sb 4*d*, Ga 3*d*, and As 3*d* as a function of the increasing Co coverage for the Co/Sb/GaAs(110) interface. (b) Evolution of the integrated intensity as a function of the Co coverage increase. Squares, open circles, and open diamonds correspond to the Sb 4*d*, Ga 3*d*, and As 3*d* core levels, respectively.

signal. Interestingly, this result is in clear contrast with previous spectroscopic studies for the Co/GaAs(110) interface [3,4], which show that the gallium signal attenuates much more rapidly than the arsenic one. For the latter, we have observed that due to the antimony treatment the As dilution in the Co films decays about twice faster than for the bare substrate due to the reduced interdiffusion [3,4]. Regarding the Ga 3*d*, the slower decay in intensity can be understood mainly due to the large increase observed for the reacted component, which accounts for the Ga atoms dissolved in the Co matrix. In summary, our study evidences that the Sb treatment inverts the interaction with respect to the bare substrate, thus reducing strongly the interaction with the As and favoring the diffusion of Ga

atoms into the Co matrix, which is accompanied by and increase of the lateral island size as observed by reflection high-energy electron diffraction (RHEED) technique [16]. This effect should lead to an increase of magnetic moment [8,21] which might be further enhanced by the Ga diffusion [9].

The characterization of the atomic structure of the Co films grown on the Sb/GaAs(110) interface has been performed by means of the structural technique x-ray photoelectron diffraction (XPD) [22]. In this study, the intensity of the Co $2p$ core level was measured as a function of the emission direction for a large set of Co films using a conventional x-ray gun with $h\nu = 1253$ eV (Mg $K - \alpha$), recording photoelectrons with an average kinetic energy of 781 eV. Systematically, typical experimental diffractograms displayed in Fig. 3 could be obtained by recording the photoelectrons at a constant angular step of 2° for both the polar (θ) and azimuthal (ϕ) angles. The polar angle, scanned by changing the analyzer position, was swept from normal to 60° off-normal emission while the azimuth was varied in a range of 180° by moving the sample manipulator. The final diffractogram displayed in Fig. 3 has been obtained by symmetrizing to 90° the recorded angular data. We have represented the normalized intensity [$\chi = (I - I_0)/I_0$] using a color scale, where the bright yellow corresponds to the highest recorder photointensity. We can observe in the diffractogram well defined spots with maxima at 44.0° ± 0.5° polar angle along the [0$\bar{1}$1] and 34.0° ± 0.5° polar angle along the [001] direction, respectively, which correspond to an average deviation of 4% with respect to the ideal forward focusing peaks depicted in panels (c) and (d) of Fig. 1. In panel 3(b), the experimental diffractogram has been plotted together with the theoretical stereographic projection expected for a perfect bcc film in order to index the observed spots. It can be noticed that the experimental forward focusing directions match quite nicely to the theoretically expected positions. Therefore, we can safely conclude that the Sb treatment considerably reduces the atomic distortion of 14% observed for the Co deposition on the bare substrate [5].

Finally, the magnetic properties of the Co grown films have been investigated by XMCD measurements at room temperature by comparing the results for both the Co/GaAs(110) and Co/Sb/GaAs(110) interfaces. In Fig. 4, we present the absorption measurements at the Co L-edge for a 18 Å Co film grown on both the bare and Sb pretreated GaAs(110) substrates. The figure displays the parallel and antiparallel orientations between the applied magnetic field and the photon spin together with the XMCD difference spectra multiplied by a factor 5 in order to better visualize the changes. Measurements were performed with the highest available magnetic field of (±400 Oe) applied parallel to the photon beam direction and forming an angle of 45° with respect to the surface normal. It was contained in the plane formed by the surface normal [110] and the in-plane [111] high symmetry directions.

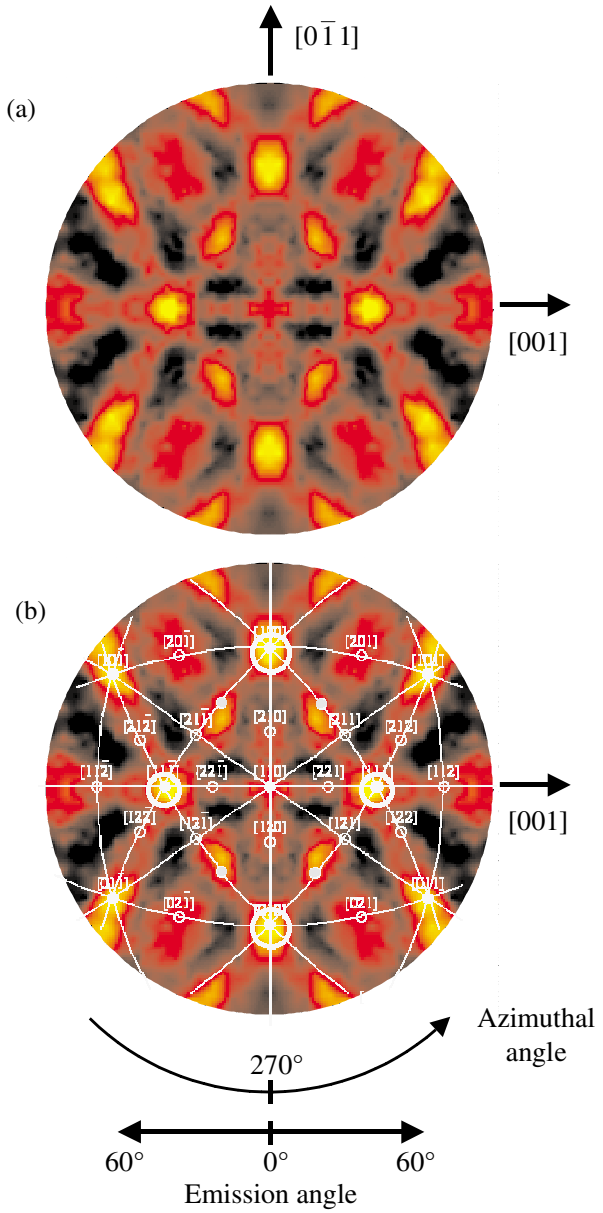

FIG. 3 (color). (a) Experimental XPD diffractogram corresponding to the Co $2p$ core level intensity modulation for a 24 Å Co film recorded with a photon of energy $h\nu = 1253$ eV (Mg $K - \alpha$). The highest (lowest) photointensity is depicted in yellow (black) color. (b) XPD diffractogram together with the theoretically expected stereographic projection for an ideal bcc film (white lines).

The results show a clear dichroic signal even for the Co films grown on the bare GaAs(110) interface. Measurements performed for lower Co coverage (not shown) indicate that a magnetic signal is clearly visible from a Co coverage of 6 Å, demonstrating that if a magnetically dead layer exists it will be much thinner than previous estimations [12]. From Fig. 4(a) we can also observe that there is no XMCD difference at the L_2 edge for the Co/GaAs(110) interface which, upon recalling the sum rules used to calculate the magnetic moment, evidences a quenching of the spin moment. Regarding the Co/Sb/GaAs(110),

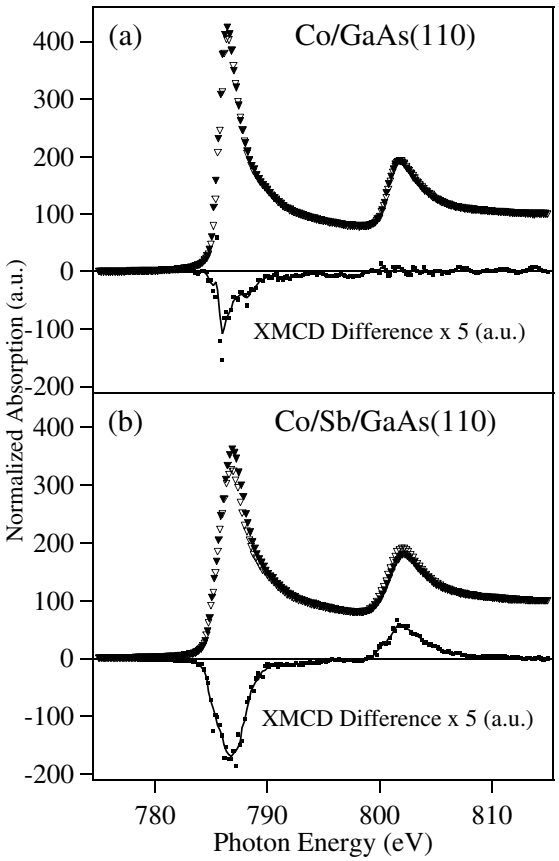

FIG. 4. Normalized dichroic absorption spectra corresponding to a parallel or antiparallel orientation between the remanence and the photon spin and XMCD difference spectra for the Co/GaAs(110) interface (a) and the Co/Sb/GaAs(110) (b). Open triangles indicate the photon spin parallel to the remnant magnetization, full triangles antiparallel. The XMCD difference has been displayed as solid squares, the solid line corresponds to the smoothed difference spectra.

we can appreciate that the magnetic contrast is much larger compared to the Co/GaAs(110) case, in spite of the Sb floating on top of the surface which should reduce the surface magnetic moment. We have estimated the ratio between the orbital and spin moment of the two interfaces and we have obtained that both contributions are enhanced by a factor 2.3 when the GaAs(110) substrate is pretreated with Sb. Furthermore, the provided measurements also prove that the films grown on Sb/GaAs(110) are magnetically softer along the [111] direction than those grown on the bare GaAs(110) substrate [1].

In summary, we have presented a very exhaustive study of the Co/Sb/GaAs(110) interface in order to unravel the role played by the Sb on interface reaction, the atomic structure, and the magnetic properties of the Co overlayers. The high resolution photoemission experiments have shown Sb to float on top of the Co overlayers for all investigated coverages, thus confirming its surfactant behavior. The latter has been established by the observed reduction of the interface reaction and the drastic improvement of the atomic crystallinity of the Co metallic films. In particular, a very slightly distorted (around 4%) bcc structure has been obtained, thus reducing the 14% reported for Co films deposited on the bare GaAs(110) substrate. The significance of the improved epitaxy on the magnetic properties evidenced by means of XMCD has allowed us to corroborate that the magnetically dead layer in this type of interface is smaller than 6 Å. Furthermore, a very large enhancement on the magnetic properties of the grown Co films is obtained when using Sb as a surfactant. Hence, we may suggest that the beneficial effect of the Sb as surfactant is mainly based on the inhibition of As diffusion, which is essentially replaced by Ga, which has much less harmful effects on the cobalt magnetization.

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