Short period magnetic coupling oscillations in Co/Si multilayers: Role of crystallization and interface quality

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In this work we show, in a transition-metal-semiconductor system, that both the interfacial quality and the crystallographic structure of the samples play an important role to allow the observation of the predicted properties of the system. To reduce the interfacial mixing, Co/Si multilayers were grown at 90 K and different crystallization qualities have been obtained by depositing the samples on glass and silicon substrates. To be able to observe experimentally the short period magnetic coupling oscillations predicted by theoretical computations, the Si spacer layers must be in a crystalline form and the interfacial mixing to be reduced to 5 atomic planes. However, the role of the crystallographic structure or growth direction of the Si layer seems to be weak. This is in agreement with the theoretical computations suggesting that the magnetic properties of such a system are driven by the presence of quantum well states at the Fermi level of the semiconductor regardless of its crystallographic structure.

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I. INTRODUCTION

Since the discovery of antiferromagnetic (AF) exchange coupling and giant magnetoresistance effect in ferromagnetic layers separated by nonmagnetic metallic interlayers,[1,2] intensive work has been focused on the magnetic and electronic properties of multilayered systems. The improvement of the techniques to elaborate nanostructured systems[3] led to the development of the so-called "spintronics."[4] More recently in particular, in order to develop magnetic random access memories (MRAM), the nonmagnetic metallic spacers have been replaced by nonmetallic spacers. While interesting results have been obtained with an insulating barrier, when the spacer is a semiconductor, the experimental results are more controversial and their theoretical interpretation is less clear. For example, in the case of the Fe/Si system, antiferromagnetic coupling has been reported but, depending on the samples, it can have an oscillatory[5] or nonoscillatory[6] behavior. The discrepancy between these results has been explained theoretically by the formation at the interface of an iron silicide layer.[7] In contrast with the Fe/Si system, Co/Si based multilayers have been much less studied. From the experimental point of view strong intermixing is always observed (of the order of 5 to 10 nm) in the form of amorphous alloys or crystalline silicide.[8,9] From the point of view of the theoretical results, only one work by Enkovaara *et al.*[10] has studied Co/Si hcp⟨0001⟩ multilayers, proposing an oscillatory behavior of the coupling showing a very short oscillation period. Similar short period magnetic coupling oscillations were also obtained by our own computations but with a Si spacer with a ⟨001⟩ diamond structure.[11,12] For both crystallographic structures the computations predict that the coupling sign does change for each additional layer in the Si spacer. This behavior is very different from the one observed experimentally when the samples are prepared at room temperature. Antiferromagnetic coupling has been reported, but no clear coupling oscillations.[13,14] These results suggest that strong diffusion processes, that are difficult to control, may be at the origin of the various magnetic behaviors that are reported. Indeed, very recently we have shown that, when prepared at low temperature (90 K), the coupling oscillations predicted by Enkovaara *et al.* can be observed experimentally.[11,12] The observation of the short period coupling oscillations has been attributed to the reduction of interfacial mixing due to the low temperature deposition. In this paper, we will show that, in addition to the necessity to reduce the interfacial mixing, a good crystallographic structure of the samples is needed to observe the short period coupling oscillations. Indeed, while all the samples show similar interfacial thickness, no coupling oscillations are observed when the Si spacer layers are amorphous. However, the role of the growth direction of the Si layer seems to be weak. This is in agreement with the theoretical computations suggesting that the magnetic properties of the system are driven by the presence of quantum well states at the Fermi level of the semiconductor, regardless of its detailed crystallographic structure.

In the first part of this paper, the detailed structural analyses of the samples are presented. In a second part, the magnetic properties of the samples showing amorphous and crystalline Si spacer layers are discussed at the light of their structural characteristics.

II. EXPERIMENTAL

The samples were fabricated in an Alliance Concept sputtering system with the following deposition conditions. The sample holder temperature was maintained at 90±5 K during the whole fabrication process, and thermal contact with the substrates was obtained by clamping the substrates to the sample holder. Before deposition, base pressure was better than 5×10^{-8} mb and, during the deposition process, Ar pressure was 5×10^{-3} mb. Deposition rates of Co and Si layers were both of 0.05 nm/s. Prior to deposition the substrates were cleaned *in situ* by argon plasma. This allows removing the native oxide of the Si substrates. Three series Si/Co mul-

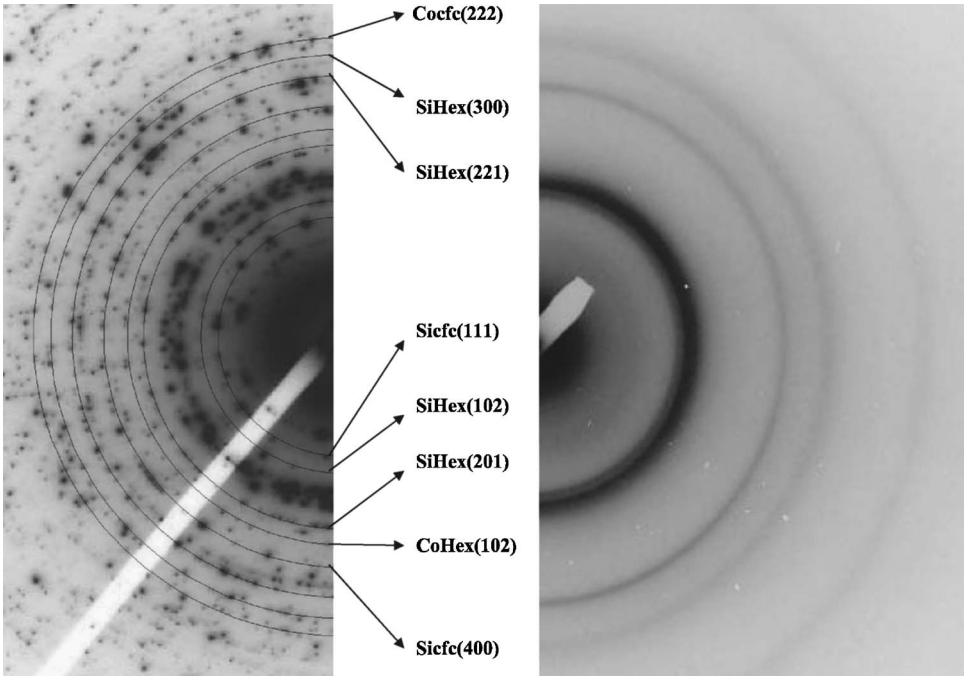

FIG. 1. Diffraction patterns of typical samples. The sample grown on Si ⟨111⟩ (left-hand side) is crystallized and shows well-defined dots. The sample grown on glass (right-hand side) shows wide unstructured rings with a diffuse halo that is typical of an amorphous contribution. The diffraction pattern can be attributed to the presence of fcc and hcp Si and of fcc and hcp Co. The drawn rings correspond to the contributions that can be attributed to only one of the phases mentioned above.

tilayers have been fabricated: Si⟨111⟩[Si4 nm/Cot_{Co} nm]*6 with 2 nm$<t_{Co}<$9 nm, Si⟨111⟩[Sit_{Si} nm/Co3 nm]*6 with 1 nm$<t_{Si}<$4 nm and glass[Sit_{Si} nm/Co3 nm] with 2.8 nm $<t_{Si}<$3.2 nm. All the samples have been protected by a 10 nm thick Si capping layer. The samples have been studied by x-ray reflectometry, TEM plane views, and by zero field nuclear magnetic resonance (NMR). The magnetic properties of the samples have been measured by a SQUID magnetometer.

III. STRUCTURAL ANALYSES

The crystalline structure of the multilayers has been studied by transmission electron microscope (TEM) plane views. No mechanical process has been used to thin the samples to allow the TEM observations. Indeed, the layers have a natural tendency to come off the substrate. The parts of the layers separated from the substrate were simply collected on the microscope grid. This ensures that no modification of the sample structure and morphology has been induced during the sample preparation prior to the TEM observation. Diffraction patterns of typical samples grown on Si⟨111⟩ and on glass substrates are shown in Fig. 1. While the diffraction pattern of the sample prepared on a Si substrate shows well-defined dots, the diffraction pattern of the one prepared on glass shows wide unstructured rings with a diffuse halo typical of an amorphous contribution. This suggests that, when deposited on glass substrates, the Si spacer layers are amorphous or composed of very small grains. An analysis of the diffraction dots and rings shows that all contributions can be identified as arising from fcc and hcp Si[15,16] and from fcc and hcp Co.[17,18] The diffraction rings that are identified in Fig. 1 are the ones that can be attributed unambiguously to only one of the four Si and Co phases mentioned above. Even if the samples deposited on Si substrates are well crystallized, no preferential growth direction has been obtained. However, the narrowness of the diffraction dots suggests a large grain size. To evaluate the lateral size of the grains, a dark field image has been established by selecting a small area of the diffraction pattern. The resulting image is shown in Fig. 2. From this image an average grain size of the order of 300 nm can be evaluated. Such a grain size is surprisingly large for sputtered sample and low temperature deposition.

To check the long range quality of the layered structure low angle x-ray reflectometry has been performed. Figure 3 shows examples of x-ray spectra for the samples deposited on Si⟨111⟩ substrates and with varying Co thickness (left-

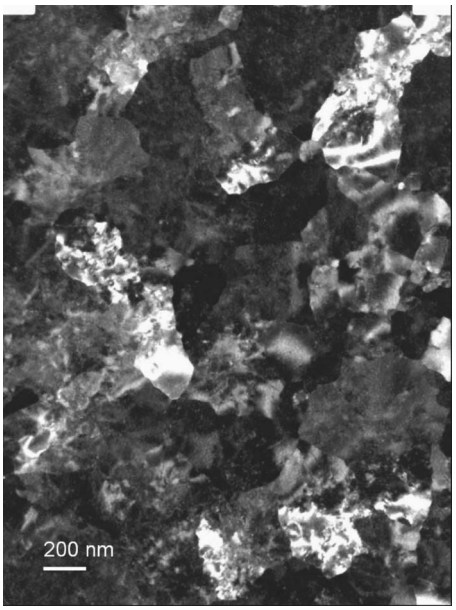

FIG. 2. Dark field image for Co/Si multilayer grown on Si⟨111⟩. The average grain size is of the order of 300 nm.

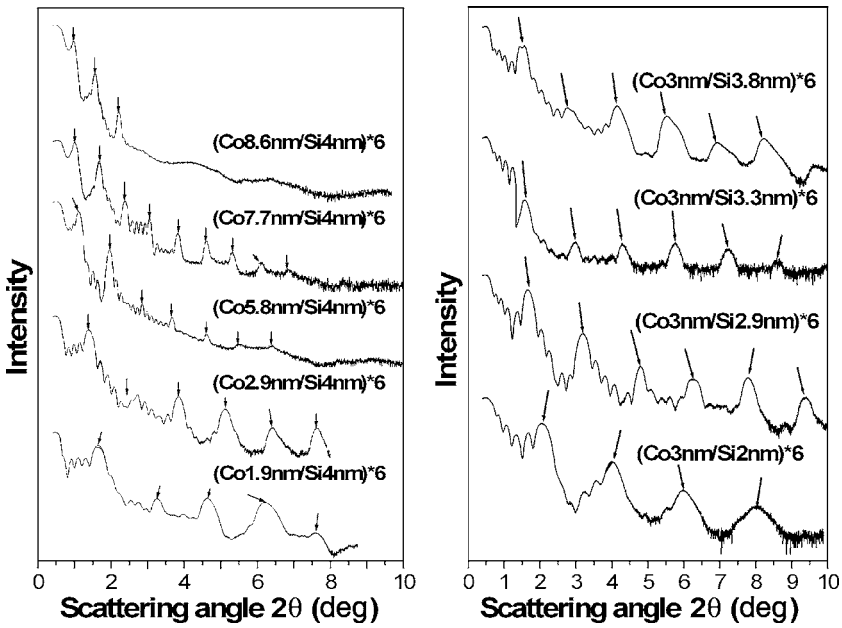

FIG. 3. Low angle diffraction patterns for samples with varying Co thickness (a) and Si thickness (b). The presence of Bragg peaks confirms well-defined multilayer structures.

hand panel) and Si thickness (right-hand panel). The small period peaks are the Kiessig fringes, and they characterize the interferences of x rays with the top and bottom of the multilayer stack. The presence of Kiessig fringes shows the good flatness of the sample surface. The satellite peaks (marked by arrows in the figure) are the Bragg peaks which originate from the interferences of x rays in the superstructure of the periodic multilayer. The presence of such Bragg peaks in our spectra is a clear evidence of the presence of a superstructure in the Co/Si multilayers prepared at low temperature. However, as seen in Fig. 3, both the Kiessig fringes as well as the Bragg peaks slowly vanish when the multilayer thickness is increased. This is observed when maintaining the Si thickness constant, as well as when the Co thickness is maintained. As often observed in multilayered systems, it suggests that the layering quality decreases with the increase of the sample total thickness. Quantitative information on the surface roughness and interface thickness can be obtained by simulating the x-ray data. The experimental results have been simulated by the program X'Pert-Reflectivity from PANalytical B. V. In this program the interfacial mixing is simulated by a linear concentration profile between the two pure elements. An example of a simulated spectrum is given in Fig. 4. From the simulation one can deduce the surface roughness and interface thickness. The top of the layers is surprisingly flat: 0.2 nm of surface roughness. This has been confirmed by atomic force microscope measurements showing an RMS roughness of the top of the layers of 0.2 nm. The interface thickness deduced from the simulation is of 0.9 ± 0.3 nm.

The low angle x-ray spectra of the samples deposited on glass substrates are very similar to the ones of the samples deposited on Si substrates, as shown in Fig. 5 for two samples with similar Co and Si thickness. It shows that both the layering quality, as well as the interfacial thickness, is similar in both kinds of samples, even though the ones deposited on silicon contain crystallized Si spacer layers, while the ones deposited on glass contain amorphous Si spacer layers.

To get a better insight into to the structure of the Co layers, and particularly into the buried Co/Si interfaces, the samples have also been studied by zero field NMR. The NMR spectra, performed at 1.5 K, are shown in Fig. 6. They are normalized to the samples surface area. As usually in multilayers the NMR spectra can be decomposed in two contributions.[19] The contribution above 210 MHz corresponds to Co atoms lying in the bulk of the Co layers (Co atoms surrounded by other Co atoms), and the contribution below 210 MHz corresponds to Co atoms in the Co/Si interfaces with Si atoms nearest neighbors. Indeed, the proximity of Si atoms depresses the resonance frequency of the Co atoms.[20] The main line resonance frequency corresponds to Co atoms in an hcp (220–225 MHz) structure while at larger Co thickness a contribution corresponding to fcc Co (216 MHz) increases. Since the NMR signal is normalized to the samples surface area, the integral area of the spectra in Fig. 6 is directly proportional to the sample surface density of magnetic Co atoms. Figure 7 shows the plot of the NMR intensity versus the deposited Co thickness. As expected for

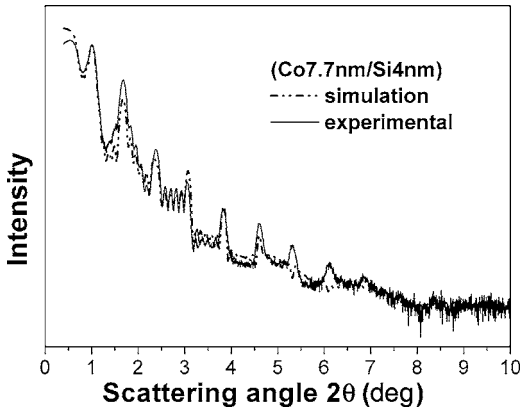

FIG. 4. Experimental and simulated low angle x-ray diffraction pattern. The deduced surface roughness is 0.2 nm and interface thickness is 0.9 nm.

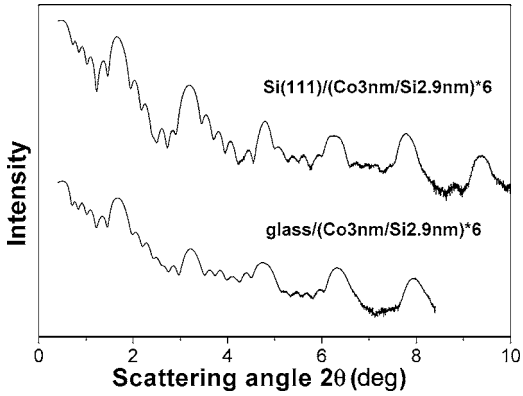

FIG. 5. Comparison of low angle diffraction patterns of a sample deposited on glass substrate and of a sample deposited on Si substrate.

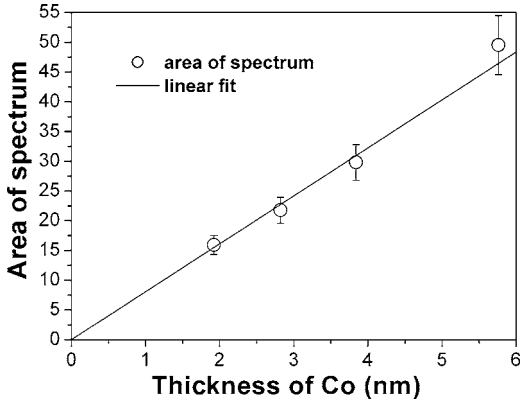

FIG. 7. Evolution of the total intensity of the NMR spectra of the Co/Si multilayers versus the deposited Co thickness. The linear fit goes through zero showing that all Co atoms are ferromagnetic.

samples with identical interface thicknesses, the intensity increases linearly with the deposited Co thickness. In addition, the fitted line does cross the origin of the plot. This means that all Co atoms are ferromagnetic at 1.5 K which suggests rather sharp interfaces. However, the broad low frequency tail (<210 MHz) observed in Fig. 6 evidences the presence of some amount of interfacial mixing since for a perfectly flat interface one single low frequency line is expected.[19] To get a more quantitative knowledge of the magnitude of the interfacial mixing, the NMR spectra have been simulated by a diffuse interface model. This model has been extensively used to simulate NMR spectra of metallic multilayers.[19] In this model the interfaces are simulated by a stacking of two-dimensional random alloys (Co/Si and Si/Co interfaces are supposed to be identical since by NMR it is not possible to distinguish them). The interface width and concentration profile is adjusted until the reconstructed spectrum fits the experimental data. In the Co/Si multilayers under investigation the obtained concentration profile is shown in Fig. 8. The simulations show that Si is mixed with Co over a thickness of 5 atomic planes and that the Si concentration profile through the mixed region is almost linear. This interface thickness is similar to the one deduced from the x-ray simulations. Since NMR is sensitive to the short range structure and x ray to long range structure, the fact that both techniques give similar results suggests that the interfacial extent is homogenous on a large scale with a very small waviness.

IV. MAGNETIC PROPERTIES AND DISCUSSION

The structural analysis of the samples shows that when prepared at low temperature the interface thickness is limited to about 1 nm compared to the 5 nm reported in the literature for room temperature deposition.[8] In addition, if Si⟨111⟩ substrates are used, it is possible to obtain well crystallized samples, and even if no preferential growth direction is inferred, the size of the crystallographic grains is very large (300 nm). Only one report of low temperature deposition of Co on top of a Si substrate has been found in the literature.[21] The samples were deposited at 150 K and their magnetic properties measured at the same temperature by a Kerr magnetometer. Interface quality was analyzed in term of magnetic dead layers: 3.5 atomic layers of Co are found to be nonmagnetic when the samples are deposited at 150 K. For sake of comparison, the saturation magnetizations, normalized to the sample area and measured at room temperature,

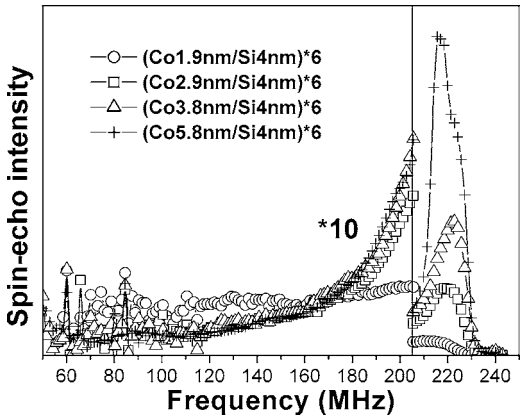

FIG. 6. ^{59}Co NMR spectra of the (Co t_{Co} nm/Si 4 nm)*6 multilayers. NMR intensities are normalized to the samples surface area.

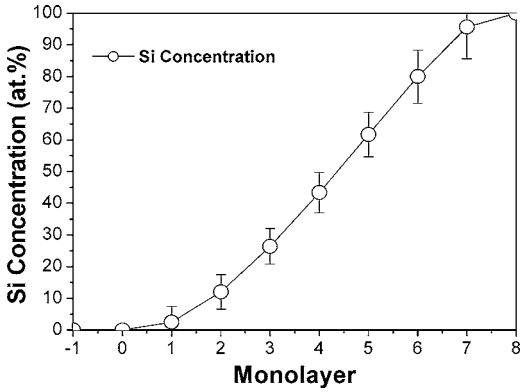

FIG. 8. Si concentration profile in the interface. The monolayer at zero corresponds to the full Co plane which is in contact with the interface. Interfacial mixing extends over five atomic planes.

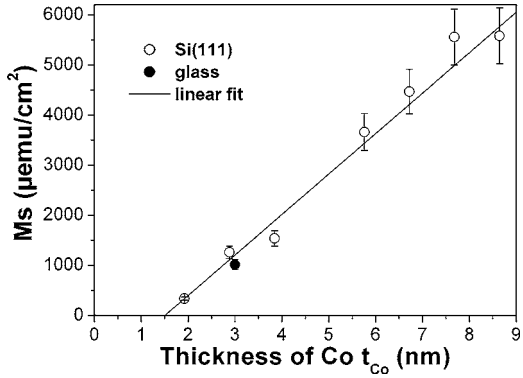

FIG. 9. Evolution of the saturation magnetization per surface area of the Co/Si multilayers versus the deposited Co thickness.

are plot versus the deposited Co thickness in Fig. 9. The amount of magnetic dead layers deduced from this plot is similar to the one reported in Ref. 21. It must be noted that our magnetic measurements where performed at 300 K, while in Ref. 21 they were performed at 150 K. The thickness of magnetic dead layers would probably be smaller if the magnetizations of our samples were measured at 150 K as in Ref. 21. Indeed, the NMR measurements have shown that at 1.5 K all Co atoms are ferromagnetic (Fig. 7). The comparison of our data with the results reported in Ref. 21 suggests that the interface thickness is further decreased when the deposition temperature is decreased from 150 to 90 K. The saturation magnetization of the samples deposited on glass is also shown in Fig. 9. Its value is similar to the one obtained for the samples deposited on Si. This confirms that both kinds of samples show similar interface mixing and differ by the crystalline structure of the Si spacers only.

Since the aim of the present work is to investigate the influence of the structure of the samples on their magnetic properties and particularly on the magnetic coupling oscillations reported in Refs. 11 and 12, we have focused the Si thickness investigation range close to the thickness of one of the antiferromagnetic coupling maxima, 3 nm. In the top panel of Fig. 10 the magnetization curves of crystalline (on Si substrates) and amorphous (on glass) samples are compared. It can be seen that while high and low saturation fields are clearly obtained for the samples deposited on Si, no variation of saturation fields is observed for the amorphous samples. This is evidenced in the plot of the energy needed to saturate the samples shown in the bottom panel of Fig. 10. This shows that limiting the interface diffusion is not sufficient to exhibit the short period coupling oscillations predicted in Ref. 10. This points out that these oscillations are strongly related to the quality of the crystallization of the Si spacer layers.

The saturation fields of the samples with amorphous Si spacer layers are lower than the saturation field of the crystalline samples with a Si thickness corresponding to the maximum of antiferromagnetic coupling, but surprisingly it is larger than the one obtained for Si thickness above and below the AF peak. Indeed, for amorphous samples or for samples constituted by very small grains, the saturation field

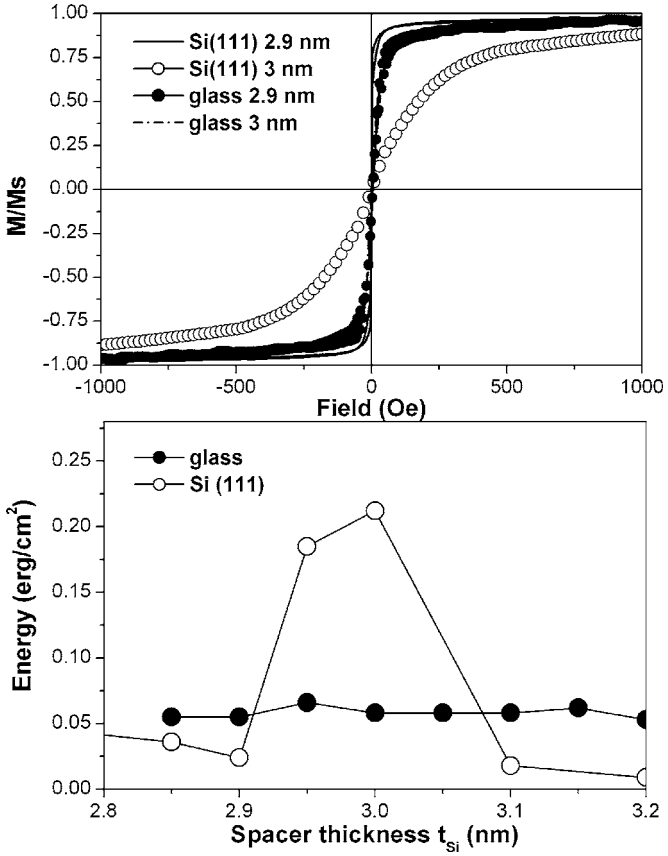

FIG. 10. Magnetic properties of the Co/Si mulilayers. Top panel: comparison of the magnetization curves of crystalline samples (on Si substrates) and amorphous samples (on glass substrates). The magnetization curves of the samples grown on glass overlap almost perfectly. Bottom panel: energy needed to saturate the samples. Amorphous samples show no coupling oscillations.

is expected to be very small. One can suggest that the observed small saturation field originates from a strong ferromagnetic coupling between the Co layers. Indeed, this might favor the nucleation of domain walls in the thickness of the samples and therefore decrease the saturation field compared to the one experienced when each magnetic layer reverses individually. Such a ferromagnetic coupling is difficult to evidence in multilayered samples, but the reduction of saturation field that is observed is consistent with a strong ferromagnetic coupling.

Finally it must be remarked that it is rather surprising that the coupling oscillations are so clearly observed in polycrystalline samples that do not even present a preferential growth direction. This, however, shows consistency with the theoretical computations since short period coupling oscillations were predicted for multilayers with very different crystallographic structures: hcp ⟨0001⟩Si and ⟨001⟩ Si with diamond structure.[10–12] In his paper Enkovaara *et al.* interprets the presence of short period coupling oscillations by the development of quantum well states at the Fermi level of the spacer. Such states are expected to develop in the semiconductor due to the absence of the band gap once the layer is embedded in the multilayer structure. Since, as remarked by Enkoraava *et al.*, this is a general trend in the transition-

metal-semiconductor multilayers, the quantum well states are likely to develop regardless of the Si structure and growth direction. This strongly supports our experimental results and makes the short period coupling oscillations a very robust property of the system as long as the Si layers are crystallized and interface mixing is sufficiently reduced.

V. CONCLUSION

The magnetic properties of magnetic-metal-semiconductor multilayers are very controversial. In this work we show that both the interfacial quality and the crystallographic structure of the samples play an important role to allow the observation of the predicted magnetic properties of such a system. In particular, for the Co/Si system under investigation, the coupling oscillations cannot be observed when the Si layers are amorphous even if the interfacial mixing is limited. Surprisingly, our results show that if the Si spacer layers are in a crystalline form, their detailed crystallographic structure or growth direction play no role on the ability to observe the coupling oscillations. This is in agreement with the theoretical computations of Enkovaara *et al.* suggesting that the magnetic properties of the system are driven by the presence of quantum well states at the Fermi level of the semiconductor. Since such states are likely to develop in many transition-metal-semiconductor systems, these results will promote experimental works in this research field.

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