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Tuning structural and magnetic properties of Fe films on Si substrates by hydrogenation processing

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ABSTRACT

In order to study specific phenomena at ferromagnetic/semiconducting interfaces, of potentially high interest in spintronics and information technology, structural aspects and magnetic properties of Fe thin films grown on Si(0 0 1) substrates by RF sputtering have been investigated using ^{57}Fe conversion electron Mössbauer spectroscopy (CEMS) and magneto-optic Keer effect (MOKE). Films of different thicknesses have been deposited either directly on crystalline Si substrates or on Cu buffer layers. An inherent Fe oxide layer is observed in all as prepared films, with a relative thickness decreasing drastically with the deposition time. The Cu buffer layer does not diminish either the interfacial diffusion or the oxidation process. An efficient method to prepare sharper oxygen- and silicon-free interfaces for an improved spin injection, via thermal treatment in hydrogen atmosphere, is proposed. Accordingly, the hydrogenation treatments are very efficient in the modification of the ferromagnetic film structure, phase composition, magnetic properties and interfacial mixing.

1. Introduction

An important topic of the present research in spintronics is related to the efficient injection of a spin-polarized current from an electrode into a semiconductor [1,2], with numerous applications related to novel spin dependent electron transport phenomena (e.g. giant magneto-resistance [3,4], tunneling magneto-resistance [5], etc.) or spin based electronic devices (e.g. spin wave logic devices [6], spin transfer torque [7–9] devices, etc.). Although magnetic semiconductor electrodes would be in principle more suitable in this respect, their main inconvenient is related to their relatively low Curie temperature [10]. An alternative solution consists in using an ordinary ferromagnetic film as electrode, with high remanent magnetization if possible, although the main breakdown is the "conductivity mismatch" [11] between the ferromagnetic (FM) electrode and the interfaced semiconductor (SC). The situation can be partially improved by using a high spin dependent resistance at the FM/SC interface [12], but the problem remains open for further achievements. Therefore, many efforts have been done in the last years for finding suitable FM/SC interfaces [13–20], requiring both convenient material combinations and negligible atomic intermixing. Fe films grown on crystalline Si (c-Si) substrates have been intensively studied [21–23] since it can represent an attractive solution, providing opportunities for integration of the interface in the conventional Si-based electronics. However, in the well-studied system of Fe films grown on c-Si substrates, the involved interface plays a key role, determining the overall structural and magnetic properties. Depending on the preparation conditions, atomic diffusion and intermixing processes can take place during the growth process leading to the so-called reaction of silicization [24–26]. Magnetically dead silicide layers [27–30] with low coercivity or even with non-magnetic character can be formed at different extends depending on the deposition method, with an expected negative impact not only on the magnetic properties of the ferromagnetic film but also on the quality of the FM/SC interface. One of the most common silicide phases formed at depositing Fe on c-Si at room temperature is the magnetic Fe_3Si compound [31], but other phases can also be formed [32].

A solution to reduce the Fe–Si intermixing process has came out observing that metallic Fe layers can be grown epitaxially, with negligible intermixing and with induced magnetic texture, on Ge(0 0 1) substrates [33]. Therefore, the growing of Fe layer on Si(0 0 1) substrates via a $Si_{1-x}Ge_x$ buffer layer has been successfully applied [34], by using the plasma enhanced chemical vapor deposition method.

The RF sputtering deposition method, although it is one of the most effective for large scale production, leads unfortunately to a strong interfacial atomic intermixing and consequently, new methods to reduce this process would be of large interest. To solve the aforementioned problem, we have considered to reduce the intermixing at the Fe/Si interface by the deposition of a buffer layer containing elements with lower diffusion coefficients relative to iron (e.g. Sb, $CrSi_2$, Au or Cu buffer layers have been mentioned in

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[35–38]). Moreover we propose a more efficient method, related to the post annealing of the RF sputtered iron films in hydrogen atmosphere at convenient temperature. Hydrogen is known as a reducing agent when reactions at relatively high temperatures (300–400 °C) occur. Previous studies revealed that the oxidation degree in thin films is considerably reduced and their crystallinity is improved via hydrogenation treatments [39,40] and hence, ferromagnetic/semiconducting interfaces more suitable for applications in spintronics would be expected.

The aim of this paper is the investigation of structural and magnetic properties of iron films deposited by RF sputtering on c-Si substrates. A detailed study of the changes induced on the deposited Fe films, by either Cu buffer layers or a subsequent annealing under high pressure of hydrogen is presented. The experimental investigation has been performed using X-ray reflectometry (XRR), conversion electron Mössbauer spectroscopy (CEMS), atomic force microscopy (AFM), magnetic force microscopy (MFM) and magneto-optic Kerr effect (MOKE) measurements.

2. Experimental details

Fe films enriched in the ^{57}Fe Mössbauer isotope have been deposited on c-Si(0 0 1) substrates. The samples have been prepared via RF sputtering in Ar atmosphere of a high purity Fe target, partially covered by small plackets of metallic Fe 95% enriched in the ^{57}Fe isotope and keeping the substrate at about room temperature (the substrate holder was maintained at constant temperature by flowing water at about 20 °C). A bottom-up configuration (bottom horizontal 2″ Fe target and top substrate at about 8 cm) was used. The RF power was 100 W (no magnetron was used), in conditions of a null self biasing potential for plasma confinement. The base pressure was in the range of 5×10^{-6} mbar, while the working pressure was about 5×10^{-2} mbar of argon (Ar flux of 40 sccm). Different deposition times – leading to different thicknesses of the films – have been considered. Two sets of samples have been obtained, one for Fe films grown directly on the c-Si substrate and the other one consisting of Fe films grown on a Cu buffer layer (similar deposition conditions were used for the deposition of the Cu layer as for the Fe film). No chemical treatments were applied to the c-Si substrate containing a native Si oxide with the intention to avoid a considerably increase of roughness, but the substrates were priory sonicated and washed in acetone and ethyl alcohol. However, both the target and the substrate surfaces were cleaned previously to the deposition by suitable etching procedures. It is important to consider that due to the lack of ultra high vacuum conditions, prior to the introduction of the high purity (99.9999%) Ar, a certain oxidation of films is expected during the deposition process.

A thermal treatment in hydrogen atmosphere at 300 °C, for 90 min, and at a pressure of about 10 bars preceded by 20 subsequent cycles of under vacuum cleaning and purging in hydrogen at a lower temperature (100–150 °C), has been applied afterwards. A commercially available volumetric Sievert apparatus provided by Advanced Material Corporation, Pittsburgh, USA was used in this respect.

The deposition time for the Fe films was of 1, 3, 5 and 8 min, respectively, whereas the Cu buffer layers were grown for just 3 min. An initial calibration concerning the relation between the deposition time and the film thickness was performed by Total Interferometry Contrast on thicker Fe and Cu films and final deposition rates were also confirmed by X-ray reflectometry, as discussed in the next section. The following sets of samples were finally obtained and analyzed:

- Si/Fe(3 nm), Si/Fe(9 nm), Si/Fe(15 nm), Si/Fe(24 nm) for Fe films deposited directly on c-Si substrates for 1, 3, 5 and 8 min, respectively.
- Si/Cu(24 nm)/Fe(3 nm), Si/Cu(24 nm)/Fe(9 nm), Si/Cu(24 nm)/Fe(15 nm), Si/Cu(24 nm)/Fe(24 nm) for Fe films deposited for 1, 3, 5 and 8 min on Cu buffer layers.

Corresponding samples treated via hydrogenation are additionally indexed by the suffix "_H".

The atomic force microscopy (AFM) and magnetic force microscopy (MFM) images have been obtained using a MFP-3D SA (Asylum Research) instrument working in non-contact mode by the two-step method [41], at a resonance frequency of 72 kHz. AFM scans have been performed in the first step, recording the topography, while MFM scans have been collected in the second step, with an increased distance between the tip and the sample. Si cantilevers covered with a Co–Cr alloy were used.

The X-ray reflectometry (XRR) measurements have been performed with a Brucker type (AD 8 ADVANCED) diffractometer working with Cu(K_α) radiation of 0.154 nm wavelength. The LAPTOS program was used for fitting the XRR patterns.

Conversion Electron Mössbauer Spectropscopy (CEMS) has been used in order to study the phase composition and the local structure of the Fe films. The measurements have been performed at room temperature, in perpendicular geometry (with the gamma radiation perpendicular to the sample plane), and the sample has been placed in a home-made gas flow proportional counter. A ^{57}Co source (Rh matrix) of about 35 mCi activity and a spectrometer working with sinusoidal waveform have been used. The least-squares fitting of the CEM spectra has been performed via the NORMOS computer program [42]. The isomer shifts are reported relative to α-Fe at room temperature.

Vector magneto-optic Kerr effect (MOKE) magnetometry measurements have been done at room temperature using a miniMOKE (AMACC Anderberg & Modéer Accelerator AB) device with the laser beam (wavelength of 640 nm) making an incident angle of 45° versus the sample plane (a 90° geometry between source and detector and magnetic field in both the sample and the incidence plane). The polarizer and analyzer are of Glan–Thompson type and the light modulation is made with a Faraday rotator (rod-like shape) working at 1000 Hz. The sample can be rotated in its own plane in order to change the direction of a possible magnetic anisotropy axis with respect to the direction of the applied field (azimuthal angle rotation).

3. Results and discussions

The thickness, density and roughness of the hydrogenated samples Si/Fe(9 nm)_H and Si/Cu(24 nm)/Fe(9 nm)_H have been estimated via X-ray reflectometry (XRR). The mass density profiles obtained from the fitting of the XRR spectra of the above samples are shown in Fig. 1. The corresponding XRR patterns (dotted line-experimental and solid curve – theoretical fit) are shown in the insets. The best fit was obtained in the frame of the following structural models: Si substrate, a thin SiO_2 layer, a Fe layer and a topmost Fe oxide layer, for sample Si/Fe(9 nm)_H and Si substrate, a thin SiO_2 layer, a Cu buffer layer, a Fe layer and an Fe oxide layer, for sample Si/Cu(24 nm)/Fe(24 nm)_H. The obtained parameters (thickness, density and roughness) are also presented in Table 1.

According to these results, it might be observed that in spite of the etching process of the substrate, a SiO_2 layer of 2–3 nm thickness remains present at the Si surface with a consistent roughness of about 1 nm, similar to the Si substrate. On the other hand, despite the hydrogenation treatment, a thin Fe oxide layer of just about