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Morphology of the asymmetric iron–silicon interfaces

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ABSTRACT

A systematic study of the iron–silicon interfaces formed upon preparation of (Fe/Si) multilayers has been performed by combination of modern and powerful techniques. Samples were prepared by thermal evaporation under ultrahigh vacuum onto a Si(100) substrate. The morphology of these films and their interfaces was studied by a combination of scanning transmission electron microscopy, X-ray reflectivity, angle resolved X-ray photoelectron spectroscopy and hard X-ray photoelectron spectroscopy. The Si-on-Fe interface thickness and roughness were determined to be 1.4(1) nm and 0.6(1) nm, respectively. Moreover, determination of the stable phases formed at both Fe-on-Si and Si-on-Fe interfaces was performed using conversion electron Mössbauer spectroscopy on multilayers with well separated Si-on-Fe and Fe-on-Si interfaces. It is shown that while a fraction of Fe remains as α-Fe, the rest has reacted with Si, forming the paramagnetic c-$Fe_{1-x}Si$ phase and a ferromagnetic Fe rich silicide (DO_3 type phase). We conclude that the paramagnetic c-$Fe_{1-x}Si$ silicide sublayer is identical in both Si-on-Fe and Fe-on-Si interfaces, whereas an asymmetry is revealed in the composition of the ferromagnetic silicide sublayer.

1. Introduction

A large amount of work has been dedicated to the growth and characterization of ferromagnetic metal/semiconductor nanostructures because of their unique physical properties for applications in Spintronics [1–8]. Particularly, a lot of this attention has been focused on the case of Fe/Si multilayer magnetic structures since they are quite compatible with Si microchip technology. However, in this type of multilayers, technical issues arise from the atomic diffusion and iron silicides formation at the Fe/Si interface during the deposition process. Indeed, iron silicides at the interfaces can affect their physical properties and possible applications [9,10]. Therefore, a characterization of the Fe–Si interfaces, including the morphology and formation of iron silicides during the deposition process, is of paramount importance.

The silicide formation at the Si-on-Fe and Fe-on-Si interfaces is known to be asymmetric [11,12,14,15]. In spite of the work done on this subject, there are contradictions in the literature; for example, the sequence of phase formation is still unclear. Different silicide phases like FeSi [16,17,14], c-$Fe_{1-x}Si$ [18,19,12], $FeSi_2$ [20,17,15] and Fe_3Si [11,21,22] have been proposed to be formed at the Fe-on-Si interface. In contrast, in the Si-on-Fe interface some authors report only the presence of the paramagnetic c-$Fe_{1-x}Si$ ($0 \leqslant x \leqslant 0.5$) [11,19,12,23], while others state that a ferromagnetic Fe rich Fe(Si) solid solution is also present [18,15,24]. The contradictions may be caused by differences in the samples used; specifically, the substrate and the number and thickness of the Si and Fe layers. It is unclear if some of the results can be assigned to single Si/Fe interfaces, or they should be ascribed to the interfaces in particular $(Fe/Si)_n$ systems.

To contribute to clarify this situation the present work deals with an exhaustive study on the morphology and composition of the Fe–Si interfaces as a function of depth. Firstly, we proceeded to study a Si-on-Fe interface on a single (Si/Fe) bilayer deposited

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on a passivated Si substrate, by means of a combination of techniques. Specifically, we performed scanning transmission electron microscopy (STEM) imaging combined with electron energy loss spectroscopy (EELS) and X-ray reflectivity (XRR) for the morphological characterization, whereas for the compositional study, angle resolved X-ray photoelectron spectroscopy (ARXPS) combined with hard X-ray photoelectron spectroscopy (HAXPES) were used. Secondly, we aimed to elucidate the differences in silicide composition existing between the Fe-on-Si and Si-on-Fe interfaces. The information on the Fe–Si interface constituents was obtained by using the isotope selective technique, conversion electron Mössbauer spectroscopy (CEMS). To this end we prepared a series of samples consisting of a triple repetition of the (Si/Fe) stack deposited on a SiO_2 substrate, containing ^{57}Fe probe layers placed at different regions in the Fe layers, and Fe layer thickness large enough to ensure that the two Si/Fe interfaces could be observed separately.

All the studied samples were prepared by thermal evaporation in the molecular-beam epitaxy "Angara" set-up [25] under ultra-high vacuum. A Si(100) substrate prepared by Shiraki method was used [26]. The background pressure was better than 1.0×10^{-7} Pa. Elements were evaporated from boron nitride crucibles. Growth rates were 0.4 nm/min for ^{57}Fe, 2.5 nm/min for ^{56}Fe and 1.7 nm/min for Si, which was checked *in situ* by high speed laser ellipsometry. Final thickness was measured *ex situ* by X-ray fluorescence. All the Fe and Si layers were deposited at room temperature (RT). After fabrication, all the studied samples were exposed to air.

2. Morphological study of the Si-on-Fe interface

The morphological characterization of the Si-on-Fe interface was performed on a single (Si/Fe) bilayer grown on a Si(100) substrate with thickness sequence Si(100)/SiO_x/Fe(18 nm)/Si(4.3 nm).

2.1. Microstructure characterization

High angle annular dark field (HAADF) STEM imaging combined with EELS was performed on the (Si/Fe) bilayer in a probe corrected FEI Titan Transmission Electron Microscope equipped with a Gatan Tridiem 866 ERS energy filter and operated at 300 kV. To prepare the transversal section with FIB for (HAADF) STEM measurements a Pt layer is deposited as a step in the process of cutting. The HAADF-STEM image (Fig. 1) reveals a good layer by layer growth in spite of some appreciable roughness observed at the interfaces. The STEM-EELS profile shows the presence of a SiO_x passivating buffer layer on the Si substrate. This buffer layer has 20(4)% oxygen content and a maximum of 35(4)% on its surface. On top of it, the Fe layer is shown to be polycrystalline with no oxygen content. An Fe layer thickness of 20(3) nm is obtained from this profile, which compares well with the nominal value of 18 nm. The Si layer deposited on the Fe one is oxygen free until the naturally oxidized SiO_2 region by contact with air. Finally the auxiliary Pt thick overlayer is observed on top. The thicknesses of the pure Si and SiO_2 layers in the upper-most deposited layer are determined by XRR in the next section.

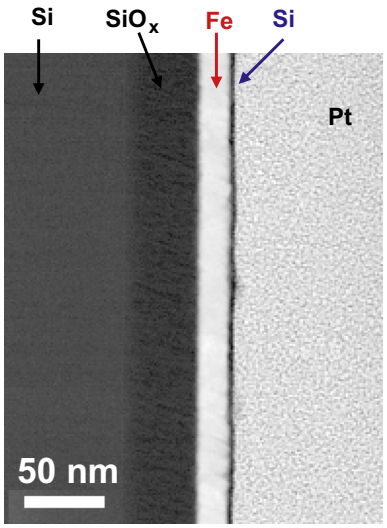

Fig. 1. HAADF-STEM image of the (Si/Fe) bilayer. A Pt layer was deposited on top of the sample for protection.

2.2. Reflectivity measurements

X-ray reflectivity (XRR) was measured on the (Si/Fe) bilayer to deepen in determining its morphology and composition. The XRR experiment was carried out at the Spanish CRG Spline beamline at the European Synchrotron Radiation facility (ESRF), using photons of a fixed wavelength $\lambda = 0.9538$ Å (13 keV). The use of high energy photon radiation allows to obtain information at larger depths than with a conventional X-ray source.

The morphology and composition of the stack can be obtained from the fit of the experimental XRR data to a layer sequence model. Specifically, the oscillations periodicity and the intensity decay in the XRR curve provide the layer thickness and roughness, respectively. The analytical software LEPTOS with a Nevot–Croce model and the Genetic Algorithm as fitting method, was used to perform the XRR fit.

The XRR experimental data and the corresponding fit (solid line) are displayed in Fig. 2. Besides the layers observed by STEM (Fig. 1), an additional layer is required to achieve acceptable fits: an iron silicide phase between the Si and Fe layers (see the stack model of Table 1). Thickness, roughness and mass density at each layer were refined, except the densities of the pure Si and Fe layers which were fixed. The fitted values of each layer forming the stack are shown in Table 1.

The XRR results reveal that the deposited Si upper layer of 4.3 nm nominal thickness is naturally oxidized ($\rho = 2.60(10)$ g/cm^3) to be compared to crystalline SiO_2 ($\rho_C = 2.65$ g/cm^3) [28], but a pure Si layer of 2.8(1) nm thickness still remains. The iron silicide layer at the Si-on-Fe interface shows a thickness of 1.4(1) nm and $\rho = 5.05(10)$ g/cm^3. This fitted density is similar to that of the stable stoichiometric ϵ-FeSi phase ($\rho = 5.19$ g/cm^3 [29]), but it also

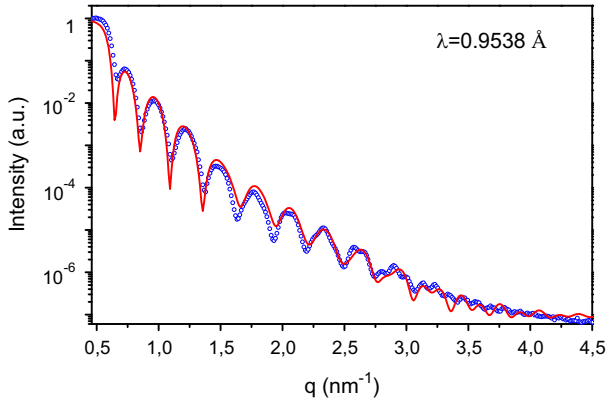

Fig. 2. XRR measurement on the Si/Fe bilayer. The experimental data are represented by the open circles while the solid line represents the corresponding fit [27]. Fitted thickness and roughness of each layer are summarized in Table 1.