Structure, reactivity, electronic configuration and magnetism of samarium atomic layers deposited on Si(001) by molecular beam epitaxy

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Abstract:

The surface structure, interface reactivity, electron configuration and magnetic properties of Sm layers deposited on Si(001) at various temperatures are investigated by low-energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS) and magneto-optical Kerr effect (MOKE). It is found that metal Sm is present on samples prepared at low temperature, with an interface layer containing SmSi_2 and Sm_4Si_3 . When samples are prepared at high temperature, much less metal Sm is found, with an increasing amount of SmSi_2 . Room temperature ferromagnetism is observed for all prepared layers, with a decrease of the saturation magnetisation when samples are prepared at high temperature. It is found that ferromagnetism implies mostly a compound with approximate stoichiometry Sm_4Si_3 . Also, the decrease in the intensity of the XAS $2p_{3/2} \rightarrow 3d$ white lines with the corresponding increasing amount of SmSi_2 may be explained by assuming a higher occupancy of Sm 5d orbitals ($5d^2$ configuration), most probably due to hybridation effects.

Keywords: samarium, samarium silicide, Si(001), MBE, LEED, XPS, X-ray absorption, MOKE

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1. Introduction

Ferromagnetic/semiconductor interfaces are widely studied in view of the emerging field of spintronics [1]. The main feature of all these systems consists of a strong intermixing of the metal with the semiconductor at the interface, no matter if this semiconductor is Si [2,3] or a III-V semiconductor such as GaAs or InAs [4]. Relatively fewer studies concentrated on the interfaces formed by 4f metals on semiconductors, despite the fact that the atomic radii of these elements (in the range or 1.8 Å) are considerably larger than that of 3d metals (1.24, 1.25 and 1.26 Å for Ni, Co and Fe, respectively) [5]. A simple, mechanistic, view of Figure 1 represents the surface primitive cell of Si(001), where the Si covalent radius of 1.11 Å was inserted [6], compared with metal atoms of the above mentioned radii. This simple picture suffices to explain the interest in depositing ferromagnetic 4f metals (such as Sm) on semiconductors [particularly Si(001)]. Although the physics of interface reactions is much more complicated and also surface reconstruction may accomodate a Sm atom into the Si mesh [2,7], one might naively expect that in this case a lower intermixing with the semiconductor occurs. A metal silicide will be formed also in this case, but one expects that the 4f metals will interact merely with the first layer of the semiconductor instead of diffusing and interacting with the deeper layers, as in the case of Fe deposited on Si [3,8].

Figure 1. Sketch of the Si(001) ideal surface primitive cell (without any reconstruction), together with atomic radii of silicon, iron and samarium. This scheme is used to explain why Fe is expected to intermix more with the Si substrate than Sm.

Samarium has several possible crystalline structures: rhombohedral (R-3m), orthorhombic (Pmmm) or hexagonal (P63/mmc). A possible forced *fcc* structure of samarium with similar density to bulk Sm would have a lattice constant of 5.15 Å and a nearest-neighbor (NN) distance of 3.64 Å. Therefore, such a structure may be stabilized on the Si(001) surface with the NN distance of 3.84 Å (see Fig. 1), since the lattice mismatch is about 5.3 %. Although bulk Sm is not ferromagnetic at room temperature, Sm atoms may provide high magnetic moments, owing to their electronic configuration ($6s^2 4f^6$). Therefore, forced, slightly inflated structures may exhibit enhanced magnetic properties [9]. Successful artificial structures of this type with 3d metals reported to date were the ferromagnetic $c(2 \times 2)$ Mn surface on Cu(001) [10] or of the forced, inflated *hcp* Cr/Ru(0001) [11]. It was also shown that enhanced magnetic properties may be obtained with Fe/InAs(001) with respect to Fe/GaAs(001), probably owing also to the larger unit cell of the substrate [12].

Sm/Si(001) provides several reconstructions for low Sm coverages; (3×2) , (2×3) obtained when Sm is deposited at high temperature (600 °C), coexisting with Sm chains [13].

It is also reported that rare earth silicides form the lowest Schottky barrier height (0.3-0.4 eV) on n-type silicon [14].

The Sm valence intervenes in a natural way, connected to the interface reactivity. There is a reported X-ray photoelectron spectroscopy (XPS) chemical shift of 7-9 eV between the divalent and the trivalent Sm, for the Sm 3d_{5/2} core level at about 1080 eV [15-17]. A similar shift (9 eV) is reported also in X-ray absorption spectroscopy (XAS) at the Sm L_{III}-edge (2p_{3/2}) located at about 6720 eV [18,19]. These reports are hard to correlate, because one might expect that chemical shifts are increasing with the binding energy of the core levels.

Consequently, it appears useful to undertake a correlated XPS and XAS study of the Sm/Si(001) interface. Also, no data are yet available about the magnetism of the Sm/Si system and this will also be addressed by magneto-optical Kerr effect (MOKE). A recent similar study was achieved in our group with the Fe/Si(001) interface [8]. It appears that, as compared with Fe/Si(001), Sm layers deposited on Si(001) exhibit lower reactivity (as expected from the naive picture of Fig. 1), better ordering and noticeable magnetism.

Two decades ago Onsgaard et al. [20] reported for Sm/Si(001) a Si 2p component shifted by almost 2 eV towards lower binding energies (BE) upon deposition of about 2 ML of Sm, attributed to the formation of Sm silicide. Annealing at 600 °C promotes a strong Sm diffusion deep inside the Si substrate. Deposition of about a quarter of a Sm ML results in an Sm 3d_{5/2} line at BE ~ 1077 eV, which was attributed to divalent Sm. More Sm deposition results in the weakening of this photoemission line and the occurrence of another line at about 1084.5 eV, attributed to trivalent Sm. Throughout this paper we will reconsider these assignments and propose that the first line should be attributed to Sm⁰ (or Sm metal) and the second line to reacted samarium (Sm²⁺, Sm³⁺).

2. Experimental

The experiments are performed in a new ultrahigh vacuum (UHV) surface science setup (Specs), composed of a molecular beam epitaxy (MBE) system with low-energy electron diffraction (LEED), connected to a X-ray photoelectron spectroscopy (XPS) chamber equipped with a conventional dual anode Al/Mg K_α source, a monochromatized Al K_{α1}/Ag L_{α2} source and a hemispherical electron energy analyzer (Phoibos 150). Resolution (in terms of full width at half maximum) of 0.85 eV may be achieved on Ag 3d_{5/2} with Mg K_α radiation and 0.45 eV are achieved with monochromatized Al K_{α1} radiation. During the XPS measurements, a flood gun operating at 1 eV acceleration energy and 100 μA electron current was used in order to achieve sample neutralisation.

Si(001) substrates are cleaned by three cycles of heating at ~ 1500 K during 30 mins in the range of 10⁻¹⁰ mbar. No oxygen contamination (i.e. below 0.1 % of a single atomic layer) was detected by XPS. Detailed experiments have shown the low contamination level promoted by XPS as compared with Auger electron spectroscopy [21]. Therefore, throughout this study, only XPS was used for contamination checks. Sharp LEED spots with both p(2×1) and p(1×2) reconstructions were observed. 3.25 ± 0.05 nm of Sm are evaporated from a Specs EBE-4 electron bombardment evaporator at a rate of 1 nm/min on substrates held at different temperatures, ranging from room temperature to 400 °C. During the evaporation, the vacuum in the MBE chamber increased to 1.4 × 10⁻⁹ mbar; however, no carbon or oxygen contamination was detected by XPS.

Freshly prepared samples were immediately covered with a 3 nm Cu layer in the MBE chamber, from a Createc effusion cell (rate 0.04 Å/s, pressure below 10⁻⁹ mbar during evaporation). These samples were investigated in X-ray absorption spectroscopy (XAS) at the A1 beamline of the Doris III ring at the Hasylab synchrotron radiation Facility, DESY, Hamburg. A Si(111) double crystal monochromator was used together with fluorescence

detection with a Passivated Implanted Planar silicon (PIPS) detector. The same samples were investigated at room temperature by longitudinal magneto-optical Kerr effect (MOKE, AMACC Anderberg and Modr Accelerator AB, He-Ne excitation).

3. Results and discussion

3.1. Low energy electron diffraction

Figure 2. Low energy electron diffraction of clean Si(001) (a), Sm/Si(001) deposited at 100 C (b), Sm/Si(001) deposited at 300 C (c). The energy of the primary electrons is given on each image. In (d), an intensity profile along the yellow line is represented by the red curve.

Figure 2 presents LEED patterns obtained on clean Si(001) and at two different deposition temperatures (100 °C and 300 °C) on the 3 nm thick Sm layer. No LEED pattern was obtained for the film deposited at room temperature, whereas the LEED pattern on the film deposited at 400 °C is quite similar to the one obtained at 300 °C. For comparison, we recall the result obtained in a study of Fe/Si(001) using the same setup [17]: (i) for substrates held at room temperature, the LEED pattern disappears completely for the lowest amount of Fe deposited (0.7 Å); (ii) a (1×1) LEED was barely visible when the deposition was performed at high temperatures (500 °C) for thicknesses lower than ~ 1 nm. Compared with these data, the case of Sm/Si(001) seems to result in a much better surface ordering. Perhaps the most interesting result is the persistence of the LEED pattern - (1×1) - also for thick Sm layers, as demonstrated in Fig. 2(c). The deposition at 100 °C results in the formation of a complicated reconstruction, possible formation of 3D islands with several facets [13]. Therefore, better surface ordering is offered by Sm/Si(001) as compared to Fe/Si(001). We turn now to the examination of the surface reactivity.

3.2. X-ray photoelectron spectroscopy

Figure 3 presents electron distribution curves of the Si 2p (a) and of Sm 3d (b) core levels for samples prepared at room temperature (RT) and at high temperature (HT, 300 °C). In Fig. 3(b) also a reference XPS spectrum on Sm₂O₃ was added (without deconvolution), obtained on a samarium sesquioxide powder pressed onto a graphite foil and measured in the same conditions as Sm/Si(001). The spectra were fitted with Voigt lines and associated integrals of the Voigt profile, both extracted from Ref. [22]. The inelastic background is associated to the inelastic scattering of photoelectrons on their way to leave the sample. Consequently, when the photoelectrons are originating from the topmost layer, one might expect that no inelastic background occurs [23]. Actually, this is the case for the "surface" components of the spectrum of Si(001) and of the component of lower BE in the spectrum of Sm/Si(001) deposited at room temperature. Therefore, we will use this "inelastic background coefficient" (IBF) as a sign to whether the emitters are located at the sample surface (when this inelastic background is very small).

Table 1. Relevant parameters of the deconvolution of Si 2p_{3/2} and Sm 3d_{5/2} core levels for Sm/Si(001) deposited at room temperature and at 300 °C. The amplitudes are normalized by the atomic sensitivity factors (ASF).

Level	Room temperature deposition				High temperature (300 °C) dep.			
	Energy (eV)	Ampli. (eV × cps)	Inel. bgnd. (eV ⁻¹)	Assign.	Energy (eV)	Ampli. (eV × cps)	Inel. bgnd. (eV ⁻¹)	Assign.
Si 2p (i)	98.37	589	0.195	Sm ₄ Si ₃	98.97	3337	0	SmSi _x
Si 2p (ii)	99.493	2222	0	SmSi ₂	99.43	3626	0.024	Si
Sm 3d (i)	1074.33	208	0.058	Sm	1074.58	83	0	Sm
Sm 3d (ii)	1081.67	1095	0	SmSi ₂	1081.22	1257	0.008	1081.22
Sm 3d (iii)	1083.83	785	0.106	Sm ₄ Si ₃	1083.17	812	0.117	1083.17

typical errors: ± 0.01 eV for energies; ± 2.5 % for amplitudes; ± 5 % for inelastic backgrounds; 0 inelastic background means lower than 10⁻⁴ eV⁻¹.

Figure 3. X-ray photoelectron spectroscopy of Si 2p (a) and Sm $3d_{5/2}$ (b). The experimental points (dots) are simulated with a combination of Voigt lines and associated inelastic backgrounds.

The deconvolution parameters are summarized in Table 1. In identifying the nature of the compounds formed at the surface, we take advantage of the following: (i) no contaminants (C,

N, O, ...) are observed in the survey spectra; (ii) it is natural to associate the lowest BE Si 2p component to Sm silicide, with the highest possible amount of Sm; (iii) it is also natural to attribute the highest BE Sm 3d component to a Sm silicide; (iv) the Sm 3d component of lowest BE (~ 1074 eV) disappears when the sample is measured for several hours in UHV, therefore it may be attributed to metal Sm [24]; (v) the highest BE Sm 3d component may be attributed to Sm^{3+} , as results from the comparison with the Sm_2O_3 spectrum; (vi) finally, no band bending was observed by measuring the valence band spectra. The data interpretation is consistent with most assignments on RE reacted with Si(001) reported in Ref. [7].

By combining everything, the most probable compositions are found as:

- a) 52 % SmSi_2 + 38 % $\text{SmSi}_{0.75}$ (Sm_4Si_3) + 10 % Sm metal for the RT sample;
- b) 66 % SmSi_2 + 30 % $\text{SmSi}_{0.75}$ (Sm_4Si_3) + 4 % Sm metal for the HT sample.

The errors in the derivation of the above atomic percentages are on the order of 1 %.

As expected, a stronger intermixing occurs when the deposition is performed at high temperature, but this yields mostly to the formation of SmSi_2 and to a fewer amount of Sm_4Si_3 .

3.3. X-ray absorption fine structure. Electronic configuration

Figure 4 presents the results of X-ray absorption measurements using synchrotron radiation on Cu capped samples. The spectra were normalized such as to provide a fixed edge jump, corresponding to a fixed total photoionization cross section towards continuum states. A straightforward observation concerns the decrease of the amplitude of the white line when the substrate temperature was increased. The total observed variation of the white line is about 20 %. This has to be connected with the observed enhanced reactivity of Sm with the Si(001), discussed in the previous Section.

The L_{III} -edge white line is a sign of $2p_{3/2} \rightarrow 5d$ transitions. It may be connected (i) to the number of 5d vacancies and (ii) to the shrinking of 5d orbitals in a more advanced oxidation state, yielding a higher superposition with the core $2p_{3/2}$ states and thus higher transition matrix elements. The first hypothesis [(i)] implies that Sm 5d orbitals may be involved in the formation of bonds with Si and could get partially filled when a larger amount of Sm reacts with Si. Therefore, the white line should be more intense for less reacted layers. On the other hand, hypothesis (ii) implies that the white line for Sm^{3+} should be more intense than for Sm^{2+} and, in general, should increase for higher ionization states.

Another hint to derive the Sm electronic configuration is provided by the 4f X-ray photoelectron spectra (not shown), which are quite similar for all samples Sm/Si(001), no matter which was the deposition temperature. The 4f line was identified at about 6.5 eV binding energy, whereas for Sm_2O_3 this line occurs at about 10 eV binding energy. According to Refs. [2,7], such a single line is a fingerprint of the $4f^5$ (^5I) configuration for Sm^{3+} . In Sm_2O_3 the Sm electronic configuration is $4f^5$ (^5D) therefore, the similitude of Sm metal and of all Sm/Si(001) low energy XPS spectra suggests that the Sm configuration is $4f^5$ [7].

Back to the X-ray absorption spectra represented in Fig. 4, the intensity ratio of the Sm L_{III} white line between the highest temperature deposited sample and the room temperature deposited sample is 0.81 ± 0.03 . We could eventually ascribe the decrease in intensity of the white line to an increasing amount of divalent Sm [2], but the 4f photoemission data preclude this assumption (no feature which may be attributed to divalent Sm is observed). Therefore, we will use mainly 5d orbital occupancy arguments. By taking into account only the hypothesis (i) outlined above and by assuming that the room temperature deposited sample, constituted mainly of Sm metal within the whole film thickness, has a $5d^0$ configuration and

therefore 10 holes in the 5d shell, it seems that samples deposited at higher temperature with stronger reactivity of Sm with silicon would have about 8.1 5d holes only. By coupling this information with the valence band photoemission spectroscopy, one derives that as soon as Sm reacts with Si, the bulklike $6s^2 4f^6$ configuration evolves progressively towards $5d^2 4f^5$ with Sm-Si reaction.

Several trials were done to derive the separate electronic configuration (the number of 5d holes) by starting with the approximate compositions derived in Sec. 3.2. However, no physical result was obtained (the resulting number of 5d holes for SmSi_2 was quite low, implying that most of outer shell electrons are on 5d states). The explanation of this fact resides in the different depth investigated by XPS and XAS. Whereas fluorescence detected XAS probes practically the whole film thickness, XPS probes about 1.5-2 nm of the outermost shell. If one takes into account the fact that the estimated thickness of 3 nm is related to bulklike Sm, the thickness of the reacted Sm silicide is larger by a factor of 2-3. Therefore, fewer information is available for deeper layers, except that there is a decrease of the number of 5d holes, most probably due to hybridization effects.

Figure 4. X-ray absorption near-edge structure (XANES) at the Sm L_{III} -edge for Sm/Si(001) deposited at different temperatures. Insert (i) represents the derivatives of the XANES spectra, used to derive the inflection points, represented in insert (ii) as a function of the deposition temperature. Insert (iii) represents the dependence of the white line intensity on the deposition temperature. The black lines in inserts (ii) and (iii) are just eyeguides.

3.4. Magneto-optical Kerr effect

All prepared Sm/Si(001) samples exhibit ferromagnetism. This is a great result in itself. Figure 5 presents two representative MOKE hysteresis loops for samples prepared at low temperature (100 °C) and high temperature (300 °C). All films exhibited ferromagnetic

properties, with a noticeable dependence of the saturation magnetization with the substrate temperature, i.e. with the reactivity: $M_s(300\text{ }^\circ\text{C}) / M_s(100\text{ }^\circ\text{C}) \approx 0.7$. By taking into account the assertions of the previous paragraph, the decrease in the Sm saturation magnetization cannot be ascribed to a decrease of the individual Sm magnetic moment (the 4f shell configuration is the same, no matter which is the deposition temperature), but rather to the enrichment in the nonmagnetic SmSi_2 phase.

For comparison, MOKE hysteresis loops obtained with exactly the same setup on Fe/Si(001) [8] exhibited a saturation signal of about 6 mdeg for 6.7 nm Fe deposited on Si(001) at room temperature, corresponding to roughly 1 Bohr magneton per Fe atom. With all the cross checks from Refs. [8,25], it was inferred that 1 mdeg of longitudinal Kerr signal corresponds to 1 nm of a Fe ferromagnetic layer with 1 Bohr magneton per atom. Therefore, if we assume that the Sm_4Si_3 phase is the main responsible for Sm ferromagnetism, the signal obtained in Fig. 5 implies also an effective Sm magnetic moment of about 2.5 Bohr magnetons per Sm atom within the magnetic compound.

One last comment regards the eventual influence of the Cu capping layer on the magnetic properties of the *in situ* prepared sample. Indeed, it was shown that capping layers may induce magnetism on islands initially not magnetically correlated [26], but in the present case, when the ferromagnetic Sm silicide is formed by a relatively strong reaction between the rare earth and the substrate, it is unlikely to suppose a consistent modification of the electronic configuration brought by the capping layer. As another argument, all data on Fe/Si(001) presented in Ref. [8], prepared in similar conditions, capped and then measured by MOKE, yielded results quite similar to uncapped samples measured *in situ*.

Figure 5. Longitudinal magneto-optical Kerr effect (MOKE) hysteresis curves of 3 nm equivalent Sm layers deposited on Si(001) at two substrate temperatures.

4. Conclusion

Room temperature ferromagnetic Sm silicide thin layers were stabilized on Si(001). The surface structure, reactivity and magnetic properties were investigated as function of the substrate temperature during deposition. The interface reactions stabilize ferromagnetic Sm_4Si_3 and perhaps also ferromagnetic Sm, together with nonmagnetic SmSi_2 . The amount of nonmagnetic phase increases when the substrate temperature is increased to several hundred °C. The nonmagnetic SmSi_2 seems to have depleted 6s states owing to a hybridization effect with Si neighbors, occupying the 5d partial density of states. The MOKE observations are in line with the observed phase composition by XPS and also with the electronic configurations derived by XAS and valence band photoemission.

Acknowledgements:

This work was financed by the Romanian National Authority for Scientific Research through Contract UEFISCDI PCCE ID 76/2010. One of the authors (RMC) is supported from the UEFISCDI Re-integration Grant RP11/2010. We acknowledge also the valuable help of the Hasylab beamline scientist Dr. Edmund Welter.

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