

Effect of carbon doping on magnetic properties of Mn/Si interface

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High-resolution photoelectron spectroscopy with synchrotron radiation and magnetic linear dichroism in Mn $3p$ core-level photoemission has been used to study the effect of carbon-doping on the initial stages of Mn/Si interface formation and its ferromagnetic ordering. It is shown that the manganese deposition on Si(100)2x1 surface with and without carbon doping results in the formation of the interfacial MnSi silicide and the solid solution of silicon in manganese. The Mn film covered with segregated Si begins to grow on the samples surface at coverage of 9 Å of Mn. It is shown that in-plane ferromagnetic ordering of the interfaces arises after of 2-4 Å Mn in both systems, however, the remanent magnetization of Mn-C/Si is higher than that of Mn/Si.

1. Introduction

Formation of magnetic films on semiconductors surfaces are of great fundamental and technological interest because they are very promising for spintronic devices. Especially much attention was paid to the magnetic semiconductors and to the silicides of transition metals, in particularly manganese silicides, which can be integrated into the standard silicon-based technology [1-3]. Despite the fact, that there is no any bulk Mn-Si phases with a Curie temperature above 50 K, ferromagnetism near and above room temperature was observed in thin Mn/Si structures formed by vacuum deposition [4] and ion implantation [5-6] methods. The high-temperature ferromagnetism was found also in discrete manganese-silicon alloys created by delta-doping [7] and for Mn_xSi_{1-x} films formed by magnetron sputtering [8] and laser synthesis [9]. The mechanism of this interesting phenomenon is still discussed. Different explanations of high-temperature ferromagnetism have been proposed as a consequence of the reduced coordination near surfaces and interfaces of silicon or due to presence of structural defects of the silicon lattice which occur in the process of preparation of the alloy [10]. Another possible reason is the presence of carbon in the grown manganese silicide film, which can results in anisotropic modification of the local structure around the Mn sites [11]. It was found that the presence of carbon in Mn_5Si_3 films enhances its Curie temperature up to maximum of 350 K [12]. However, the thickness of formed films was about 100 nm, and the influence of carbon on the magnetic properties of ultrathin films was not revealed. The aim of the present work was to study the role of carbon doping in high-temperature ferromagnetism of Mn/Si interface. We have investigated the initial growth (up to 2 nm)



of both pure and carbon-doped manganese films on silicon and for the first time studied their magnetic properties *in situ* using magnetic linear dichroism (MLD) in Mn 3*p* photoemission.

2. Experimental

The experiments were carried out in the Russian–German laboratory at the electron storage ring HZB BESSY II under ultra-high vacuum (UHV) conditions (10^{-10} mbar). The samples were prepared from phosphorus-doped ($1 \Omega/\text{cm}$) silicon wafers misoriented by $\sim 0.1^\circ$ relative to the (100) plane. The Si surface was routinely cleaned by *ex situ* chemical processing followed by heating to 1450 K in UHV. This procedure provided the atomically clean reconstructed surface, which is characterized by the clear low energy electron diffraction pattern of the type Si(100) 2×1 . Manganese films were deposited on the silicon substrates from a thoroughly degassed source. Carbon doping of the films was carried by the use of C_3H_6 adsorption during Mn deposition. The pressure of gas was 10^{-8} mbar that provided the concentration of carbon of about 15%.

The phase composition and the electronic structure of the films were analyzed by high-resolution photoelectron spectroscopy with synchrotron radiation. The photon energy was varied from 110 to 600 eV, but most of the spectra were measured at 130 eV, an energy at which the surface sensitivity of the Si 2*p* spectra is maximum. The overall energy resolution of the analyzer and the monochromator was set to 100 meV full width at half maximum.

The magnetic properties of the interfaces were analyzed by magnetic linear dichroism in Mn 3*p* photoemission. This effect consists in that the energy position and shape of the Mn 3*p* peak measured within a narrow solid angle depends on the direction of sample magnetization. The origin of the effect lies in the splitting of the spin-orbit doublet, $3p_{1/2}$ and $3p_{3/2}$, into sublevels with different magnetic quantum numbers, which is induced by core-level interaction with the magnetically polarized valence band [13-17]. The samples were magnetized along the two opposite directions lying in the plane of the sample surface by two Helmholtz coils placed inside a vacuum chamber. Current pulses passing through the coils generated a magnetic field of 1000 Oe to saturate the sample magnetization. The measurements of the Mn 3*p* spectra were performed in remanence at room temperature.

3. Results and discussion

The representative Si 2*p* and valence band spectra taken at increasing doses of Mn deposited on Si(100) 2×1 with and without carbon doping are shown in Fig. 1.

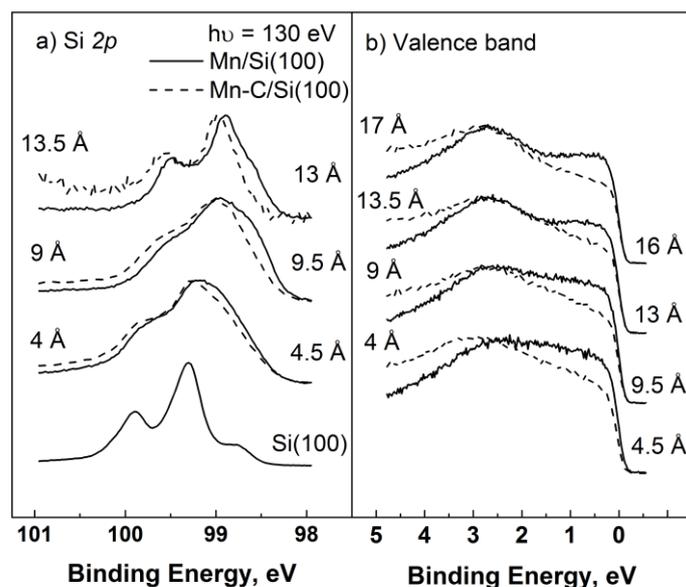


Figure 1. Si 2*p* (a) and valence band (b) spectra measured after the deposition of similar amounts of manganese on Si(100) 2×1 surface with (dashed lines) and without carbon doping (solid lines).

The dynamics of change in these spectra for both systems is very similar. For better comparison the spectra are normalized to the maxima of the curves. It is seen that the line shape is quite sensitive to the Mn deposition that reflects a change in the state of silicon atoms in the analyzed surface layer and the formation of phases with the participation of Si, Mn and C atoms in the interface region.

More detailed information on the interfaces formation can be obtained by using the least-square fitting procedure, in which the spectra are decomposed into surface and bulk components. The results of such analysis for the undoped Mn/Si system are described in our recent paper [18]. Decomposition of Si 2*p* spectra measured for carbon-doped system is shown in Fig. 2. It is seen that after the deposition of 4 Å of manganese the spectrum consists of four modes. It is the mode B that corresponds to the bulk silicon atoms and three components (I, C and S) with binding energies equal to 99.55, 99.00 and 98.67 eV, respectively. These binding energies are close to the values obtained for Mn/Si interface corresponding to interfacial MnSi silicide, the film of a solid solution of silicon in manganese and the silicon segregated on the sample surface. Thus, in the case of Mn-C/Si interface I, C and S modes should be attributed to the Mn_{1-x}C_xSi silicide, Mn-C-Si solid solution and the segregated silicon.

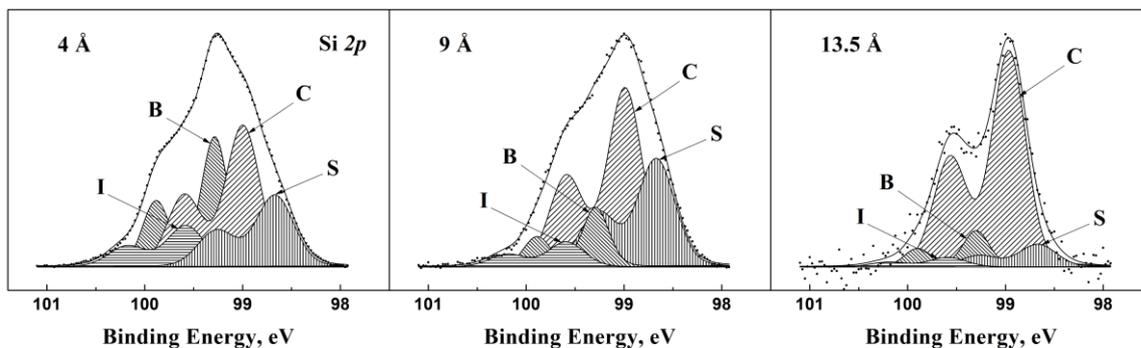


Figure 2. Decomposition of the Si 2*p* spectra from the Mn-C/Si sample with different amounts of Mn deposited at room temperature.

Based on the experimental dependences of intensity of all modes of Si 2*p* spectra on the coverage, we estimated the thickness of all layers forming the interface by assuming an exponential decay of the signal from each layer with its depth. The obtained data showed that at the early stage of manganese deposition the ultrathin layer (2.1 Å) of interfacial Mn_{1-x}C_xSi silicide is rapidly formed on the silicon surface. Then Mn-C-Si solid solution begins to grow on this layer. After the deposition of 9 Å of Mn its growth is slowing down due to the beginning of the formation of Mn_{1-x}C_x film. The manganese surface is covered with 0.2 monolayer (ML) of segregated silicon. Thus described model of the interface formation is very similar to the model that we obtained in the absence of carbon doping. The main difference between two systems is decrease of the amount of silicon segregated on the sample surface from 0.4 ML for Mn/Si system to 0.2 ML for carbon doped one.

Let us now consider the magnetic properties of the formed films. The Mn 3*p* spectra taken after the deposition of various amounts of manganese for two opposite directions of the magnetic field (*M*_{up} and *M*_{down}) for Mn-C/Si system are shown in the left part of Fig. 3. The spectra measured in the “up” direction are characterized by the picks slightly shifted to the higher binding energies in compare with *I*_{down} spectra.

To reveal the differences between the spectra we plotted the difference curves (*I*_{up} – *I*_{down}) that are shown in Fig. 3b. The difference curves demonstrate the maximum and the minimum corresponding to the sublevels of Mn 3*p* multiplet with different magnetic quantum numbers *m_j* = ±3/2. The MLD effect is commonly characterized by the magnetic asymmetry amplitude (*A*):

$$A = [S(E)_{\max} - S(E)_{\min}] \times 100\%, \quad (1)$$

$$\text{where } S(E) = [I_{\text{up}}(E) - I_{\text{down}}(E)] / [I_{\text{up}}(E) + I_{\text{down}}(E)] \quad (2)$$

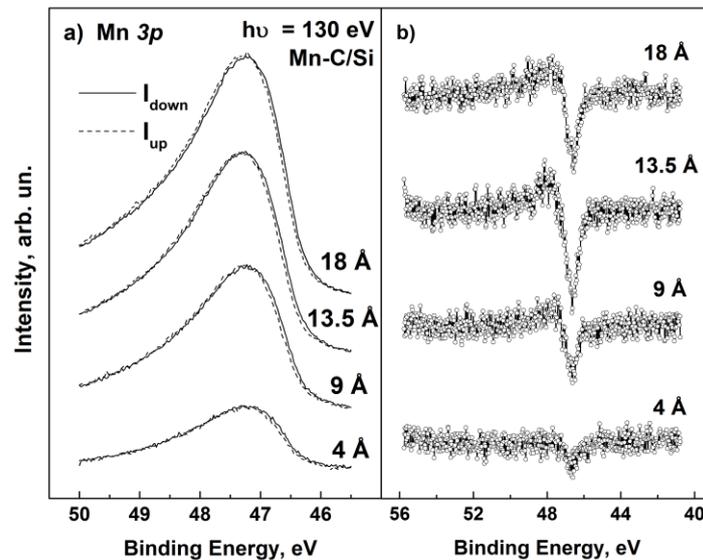


Figure 3. Mn 3p spectra $I_{up}(E)$ and $I_{down}(E)$ measured after the magnetization of the sample in two opposite directions in the surface plane (a) and the corresponding difference curves $I_{up} - I_{down}$ (b).

The parameter A is a direct measure of the sample remanent magnetization [16, 17]. Experimental data illustrating the dependence of A on the manganese coverage for both investigated systems are shown in Fig. 4.

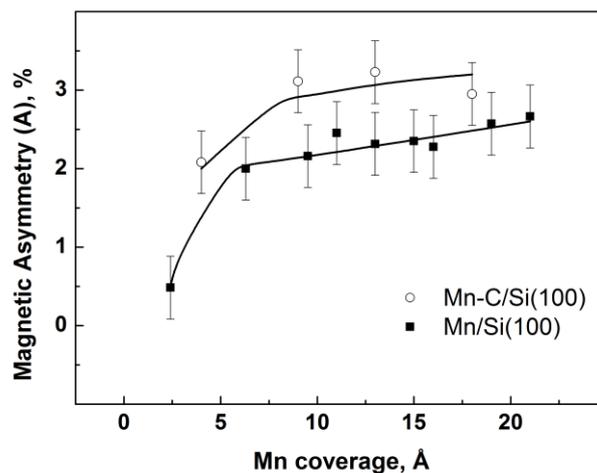


Figure 4. Magnetic asymmetry amplitude as a function of manganese coverage for Mn/Si and Mn-C/Si systems.

It is seen that the MLD effect appears in the range of 2-4 Å in both cases and enhances with increasing coverage. For example, at Mn coverage of 13 Å the value of magnetic asymmetry amplitude for undoped system becomes equal to 2.2% while for carbon-doped system it is approximately 30% higher than that for undoped one. Thereby our results demonstrate the influence of carbon on ferromagnetic ordering of ultrathin (up to 2 nm) manganese films on silicon surface.

4. Conclusion

Thus, the use of photoelectron spectroscopy with synchrotron radiation and MLD effect in the frame of a single experiment allowed us to reveal the specific features of both the formation of Mn/Si and Mn-C/Si interfaces and their ferromagnetic ordering. It is shown that the initial stages of growth of the carbon-doped and undoped manganese films are very similar. In both cases formation of interface

silicide and Mn-Si solid solution precedes the growth of a metal film. The main difference is reduction of segregated silicon on the sample surface in carbon-doped system. The high-temperature ferromagnetic ordering arises in both systems at the coverage of 2-4 Å Mn. The magnetic asymmetry amplitude of the MLD effect is equal to 3 and 2.2% for carbon-doped and undoped films correspondingly that demonstrates essential influence of carbon on magnetic properties of the films.

Acknowledgments

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