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LOW-DIMENSIONAL SYSTEMS

Solid-Phase Synthesis of Manganese Silicides on the Si(100)2 × 1 Surface

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Abstract—The solid-phase synthesis of manganese silicides on the Si(100)2 × 1 surface coated at room temperature by a 2-nm-thick manganese film has been investigated using high-energy-resolution photoelectron spectroscopy with synchrotron radiation. The dynamics of variation of the phase composition and electronic structure of the near-surface region with increasing sample annealing temperature to 600°C, has been revealed. It has been shown that, under these conditions, a solid solution of silicon in manganese, metallic manganese monosilicide MnSi, and semiconductor silicide $MnSi_{1.7}$ are successively formed on the silicon surface. The films of both silicides are not continuous, with the fraction of the substrate surface occupied by them decreasing with increasing annealing temperature. The binding energies of the Si 2*p* and Mn 3*p* electrons in the compounds synthesized have been determined.

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1. INTRODUCTION

Thin films of manganese silicides grown on a silicon surface are of considerable interest for scientists engaged in spintronics research [1]. Their application to development of magnetic structures requires, however, an adequate understanding of the processes involved in interaction of Mn atoms with the silicon surface, as well as of the reactions proceeding in the Mn/Si system at elevated temperatures. The interest of researchers dealing with the problem of synthesis of manganese silicides on single-crystal silicon has been focused until recently on the region of low coverages (from submonolayer to a few Mn monolayers) [2–10]. In some publications, the thickness of deposited films was reported to be varied in the range from several tens to several hundreds of nanometers [11, 12]. To our knowledge, however, no studies have been performed thus far in the intermediate coverage region (1–3 nm), which offers a broad array of applications. In the present work, we have attempted to fill in this gap by studying thermostimulated silicide formation reactions proceeding in the Mn/Si(100)2 × 1 system upon annealing of a 2-nm-thick manganese film deposited on the silicon surface at room temperature.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The experiments were performed at the Russian–German Synchrotron Radiation Laboratory at the HZB BESSY II beamline in ultrahigh vacuum (10^{-10} mbar). The technique employed in preparation of samples with the atomically clean Si(100)2 × 1 surface, followed by Mn deposition on them, was described in [13]. The manganese silicides were prepared by solid-phase epitaxy in isochronous (5 min) annealings of the samples coated by the Mn films. The annealings were performed at fixed temperatures raised in the course of the experiment stepwise in the range from room temperature to 600°C. The elemental and chemical compositions of the silicides thus synthesized were evaluated by high-energy-resolution photoelectron spectroscopy [14]. This was done by measuring series of spectra of silicon (Si 2*p*) and manganese (Mn 3*p*) core electrons, as well as of valence band electrons, which were excited by 130-eV photons. This selection of energy provided the maximum surface sensitivity of the method. The measurements were conducted with a CLAM spectrometer combined with a 200-mm hemispherical analyzer. The energy resolution of the instrument (accounting for the monochromator) was 100 meV.

3. RESULTS AND DISCUSSION

We consider first how the changes coming about in the near-surface region of a sample in the course of thermostimulated reactions become manifest in the spectra of photoexcited electrons. The results obtained in our study are visualized in Fig. 1 showing

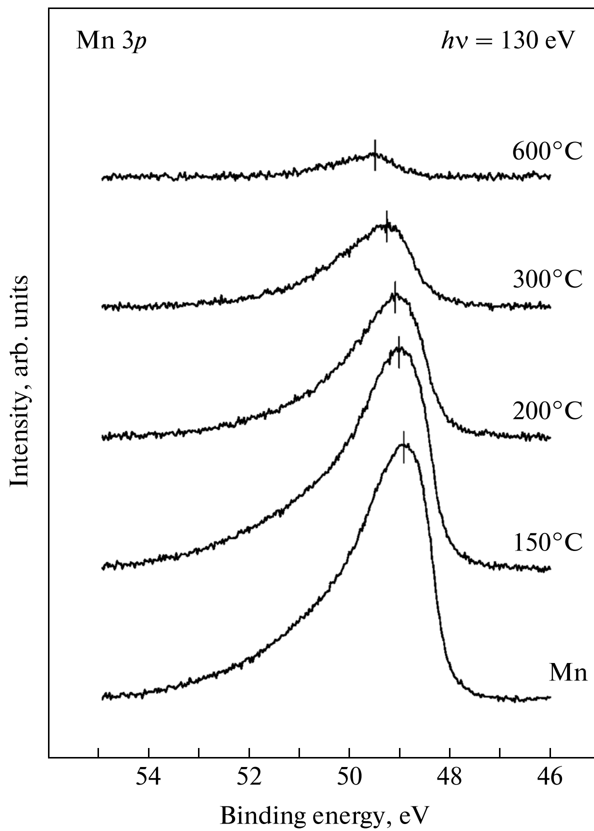

Fig. 1. Manganese 3*p* electron spectra measured after deposition of a 2-nm-thick Mn film on the Si surface and subsequent annealings of the sample at different temperatures.

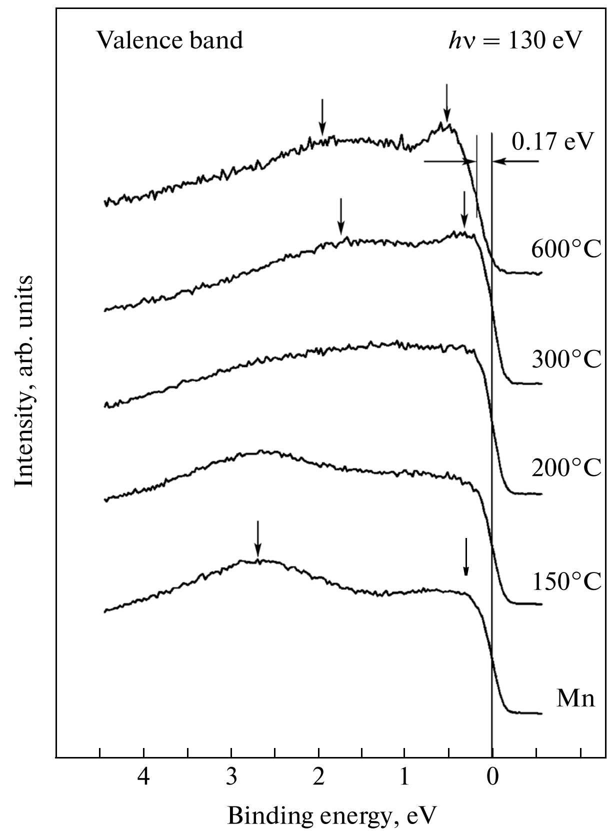

Fig. 2. Valence band electron spectra measured after deposition of a 2-nm-thick Mn film on the Si surface and subsequent annealings of the sample at different temperatures.

spectra of Mn 3*p* electrons measured after deposition of a 2-nm-thick Mn film on the Si(100)2 × 1 surface and four subsequent annealings performed at different temperatures. We readily see that the spectral line of interest obtained from the original film is a broad asymmetric maximum peaking at a binding energy of about 49 eV. Annealing the sample at 150°C brings about an insignificant decrease of the line intensity, as well as its slight displacement into the high binding energy domain, which evidences the onset of thermostimulated processes. Further increase of temperature makes the above pattern more pronounced. Indeed, following annealing at 300°C the maximum of the spectrum of the Mn 3*p* electrons is observed to shift to 49.4 eV, and annealing at 600°C shifts it to the energy of 49.65 eV. This is accompanied by dropping of the line intensity 11 times compared to its original value.

The dynamics of variation of the valence band spectra with increasing annealing temperature is illustrated by the data displayed in Fig. 2. The spectrum measured immediately after deposition of the manganese film is presented at the bottom. It reveals clearly two maxima at energies of ~0.3 and 2.5 eV, which are typical of metallic manganese. Annealing the sample at a temperature of 150°C does not practically affect the pattern of the valence electron spectrum. It changes noticeably only after annealing at 200°C, which brings about an increase of the emission intensity of electrons within the energy range from the Fermi level to 2 eV. Subsequent annealing of the sample at a temperature of 300°C is accompanied by evolvement of new features (the maxima located at 0.35 and 1.7 eV), which are typical of the spectra of valence band electrons of the manganese monosilicide MnSi [15]. This gives us grounds to believe that it is this compound that forms at the given temperature in the near-surface region under analysis. Finally, one more characteristic stage of the silicide formation process observed at the temperature of 600°C. As seen from Fig. 2, this annealing displaces the upper edge of the valence band into the energy region below the Fermi level. The magnitude of the shift is 0.17 eV, which demonstrates clearly the variation of the electronic properties of the near-surface sample region, which becomes a semiconductor. Because the only semiconducting manganese silicide is the $MnSi_{1.7}$ compound, one comes to the conclusion that it is this manganese silicide that it is this silicide that formed under the given conditions on the surface of the sample. The above conclusion fits nicely to the available data [12, 16].

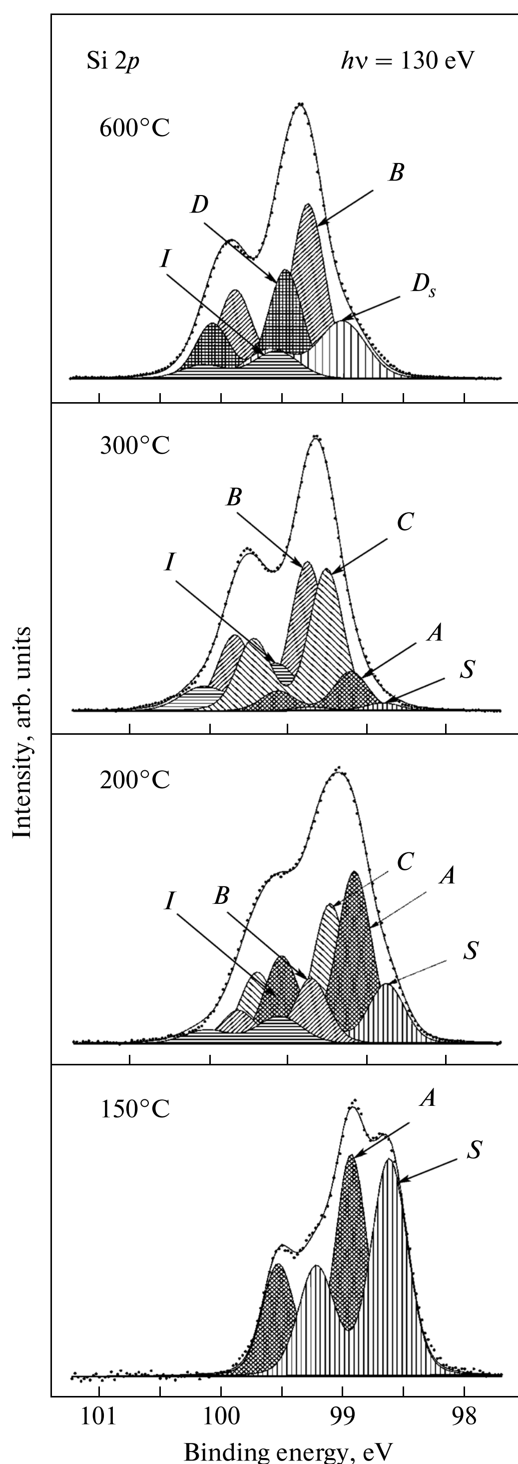

Fig. 3. Silicon 2p electron spectra measured after annealings of the sample at different temperatures and the results of their deconvolution.

As a pictorial evidence for the realization of thermostimulated solid-phase reactions in this system may serve the appearance in the photoelectron spectrum of the line of Si 2p electrons which damped completely after deposition of the Mn film on Si. This line became observable again after the sample was annealed at the temperature of 150°C, which fits the variations of the Mn 3p spectra discussed above, which signaled the onset of the solid-phase reaction. The dynamics of the variation of Si 2p spectra with increasing temperature is displayed graphically in Fig. 3. Information on the variations of the phase composition of the near-surface region being analyzed was gained by deconvolution of the measured spectra into their components, which was performed by the standard procedure described, e.g., in [17]. The results obtained in this deconvolution are also illustrated in Fig. 3. We readily see that the line of the Si 2p spectrum measured after the sample was annealed at 150°C consists of two modes, A and S, characterized by binding energies 98.90 and 98.59 eV. A comparison of these values with similar data obtained by us earlier in investigation of the process of Mn/Si interface formation [13] suggests strongly that the observed modes are associated with the solid solution of silicon in manganese (Mn–Si) and segregated silicon. Whence it follows that the process of silicide formation starts with mutual diffusion of silicon and manganese atoms. We note also that segregation of silicon on the surface of a sample may stem from the free energy of its surface being lower than that of the metal [18, 19].

As seen from Fig. 3, an increase of the annealing temperature up to 200°C brings about a substantial change of the shape of the Si 2p spectral line, which is caused by the significant weakening of the modes of segregated silicon and Mn–Si solid solution, as well as by the appearance of three new components. This is, first, mode B of volume silicon (99.25 eV). The presence of this mode evidences partial baring of the substrate surface in the course of the annealing. Second, this is mode I of the interface manganese silicide (99.52 eV) which is crossed by the photoelectrons emitted by the partially bared regions of the substrate on their way to the surface [13]. Finally, the third component of the spectrum is mode C with a binding energy 99.11 eV. It persists under the next annealing of the sample at the temperature 300°C, which is accompanied by further decrease of the intensity of the solid solution modes and of segregated silicon. Because in these conditions, as pointed out earlier, it is manganese monosilicide that forms on the sample surface, the new component C may be the mode of the synthesized MnSi. Note that the intensities of modes B and C in the spectrum corresponding to 300°C (Fig. 3) are close to being equal. Considering that the thickness of the starting manganese film (2 nm) and, hence, that of the layer of synthesized MnSi exceeds the escape depth of Si 2p electrons, which is ~1.5 nm, it can be shown that the manganese silicide film covers about 65% of the substrate surface area.

Finally, annealing of the sample at 600°C gives rise to further variation of the shape of the line of the Si 2p spectrum. Mode B becomes amplified, which evidences increase of the area of the substrate surface not coated by the manganese silicides. Note also disappearance of