

## Initial Growth Stages of Manganese Films on the Si(100)2 × 1 Surface

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**Abstract**—Initial growth stages of manganese films on the Si(100)2 × 1 surface at room temperature have been investigated using high-energy-resolution photoelectron spectroscopy, and the dynamics of the variation in their phase composition and electronic structure with the coverage growth has been revealed. It has been shown that the interfacial manganese silicide and the film of the solid solution of silicon in manganese are sequentially formed under these conditions on the silicon surface. The growth of the metal manganese film starts after the deposition of ~0.9 nm Mn. Segregation of silicon on the film surface is observed in the range of coverages up to 1.6 nm Mn.

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### 1. INTRODUCTION

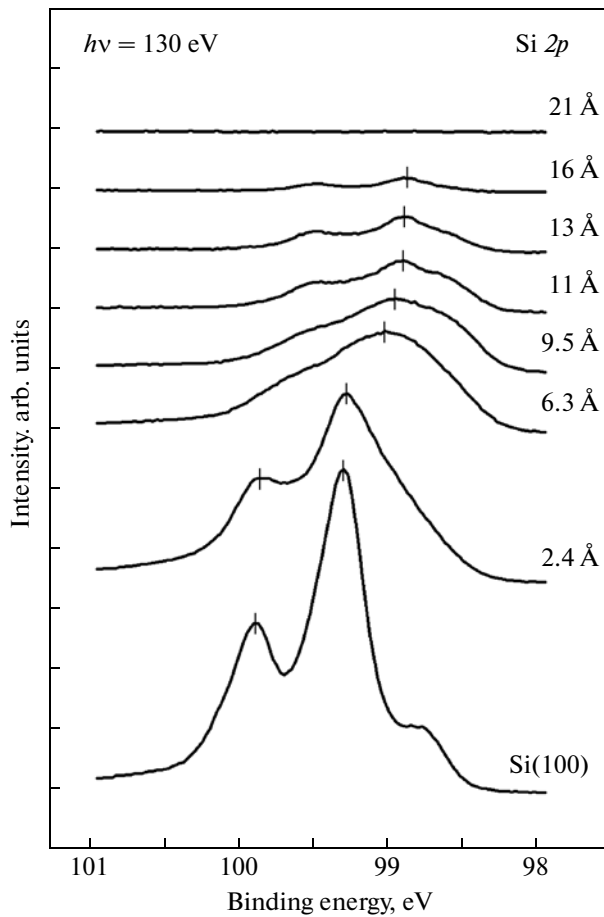
Silicides of transition metals show great variety of physical properties; therefore, they are of considerable interest both for the fundamental science and for practical applications. Thin films of these compounds already find broad application in modern microelectronics and nanoelectronics, optoelectronics, microsensors, photovoltaics, and other spheres [1, 2]. These materials are also very promising for spintronics, since, on the one hand, they can be integrated into standard elements of silicon-based semiconductor structures, and on the other hand, the transport of spin-polarized electrons can be organized in them. In connection with this, great attention is currently paid to manganese silicides [3–5]. Although these compounds either have a very low Curie temperature ( $T_C$ ) or are nonmagnetic in a bulk phase, they can possess high-temperature ferromagnetism in thin layers. Theoretical evaluations of  $T_C$  performed for metastable MnSi layers with the structure of the  $B2$  type stabilized by the Si(100) surface showed that this temperature for films one and two monolayers thick can reach 241 and 328 K, respectively [6].

The formation of manganese-based magnetic structures requires detailed knowledge of the interaction of Mn atoms with the silicon surface as well as of the reactions occurring in the Mn/Si system at elevated temperatures. These problems were considered in a number of articles, the authors of which investigated the growth of manganese films on the Si(111)7 ×

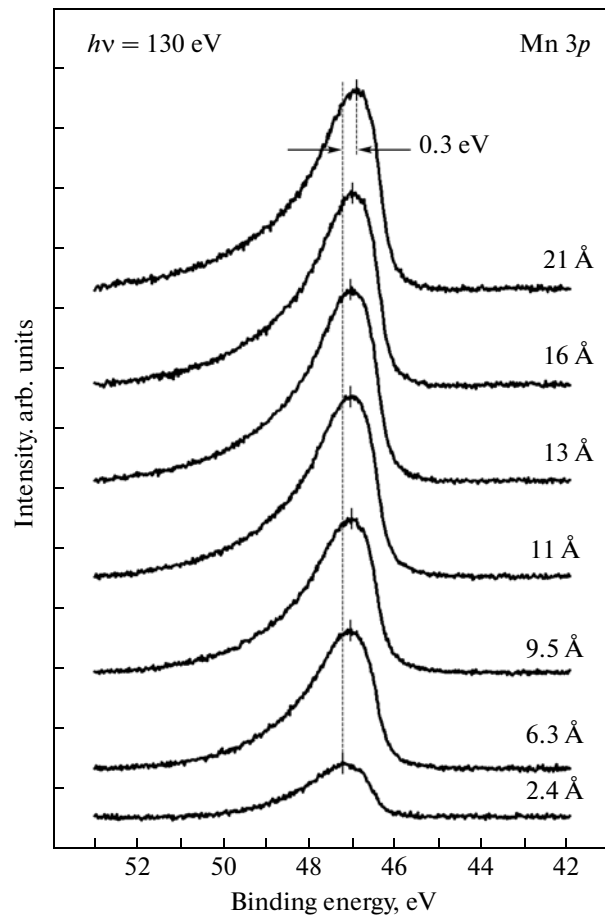
7 surface and the formation of MnSi(111) thin layers on it by the solid-phase epitaxy in detail [7–11]. In this article, we present the results of the investigation into initial growth stages of the Mn films on another silicon face, i.e., Si(100)2 × 1, which was not adequately studied. Using high-energy-resolution photoelectron spectroscopy, we revealed the evolution of the variation in the phase composition of the film with the coverage growth for the first time.

### 2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The experiments performed in conditions of ultra-high vacuum ( $10^{-10}$  mbar) were carried out using the Russian–German beamline of the synchrotron radiation at the HZB Bessy II electron storage ring. Silicon samples used as the substrates were prepared from 60KDB5–10 single-crystal silicon plates ( $p$ -type B-doped Si). The deviation of the crystallographic orientation of the samples from the (100) face did not exceed  $0.2^\circ$ . The silicon surface was cleaned by the standard method, namely, initially by the chemical treatment *ex situ* using the Shiraki method [12] and then by the high-temperature heating in deep vacuum. This procedure provided the preparation of the atomically clean reconstructed surface, which is characterized by the clear low-energy electron diffraction pattern of the type Si(100)2 × 1. The cleanness of the sam-



**Fig. 1.** Si  $2p$  electron spectra obtained for various deposition doses of manganese on the Si(100) $2 \times 1$  surface at room temperature.



**Fig. 2.** Mn  $3p$  electron spectra measured upon the deposition of Mn on silicon.

ple surface was also monitored using photoelectron spectroscopy at the exciting photon energy of 600 eV.

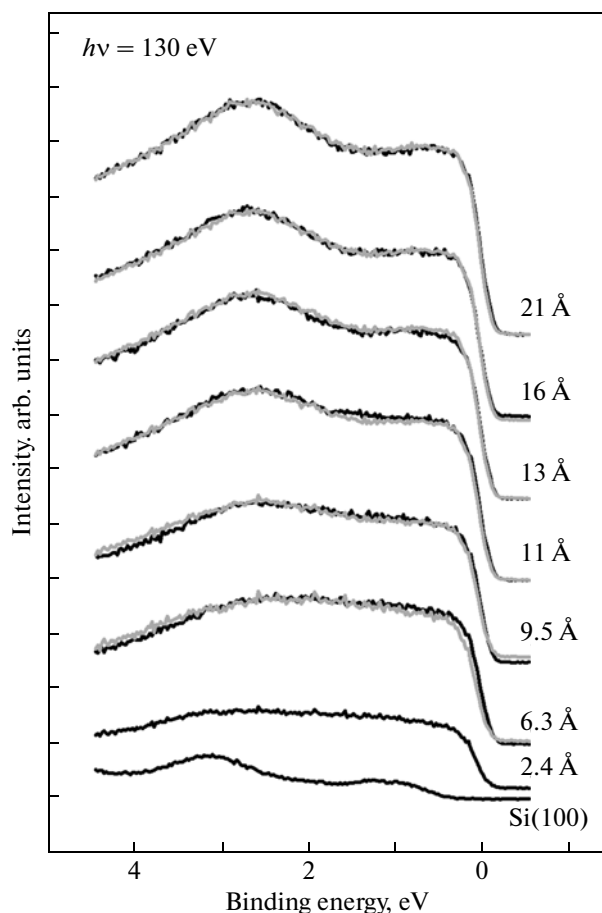
Manganese was deposited on the silicon surface at room temperature from the carefully degassed source, in which the crucible with the evaporated metal was heated by the electron bombardment. The deposition rate of Mn was approximately  $0.5 \text{ \AA}/\text{min}$ , while the coverage varied in a range from 0 to  $20 \text{ \AA}$  with a step of  $\sim 2 \text{ \AA}$ . After each deposition, we recorded a series of the core photoelectron spectra of silicon (Si  $2p$ ) and manganese (Mn  $3p$ ) as well as the valence band spectra, which were excited by photons with energy of 130 eV. This choice of the energy provided the maximal surface sensitivity of the method. The measurements were performed using a CLAM spectrometer equipped with a 200-mm hemispherical analyzer. The energy resolution of the device (allowing for the monochromator) was 100 meV.

### 3. RESULTS AND DISCUSSION

The dynamics of the variation in the most characteristics lines of the photoelectron spectrum with the

coverage growth is illustrated by the data presented in Figs. 1–3. The first of them shows several typical spectra of  $2p$  electrons of silicon measured at various formation stages of the manganese film on silicon at room temperature. The bottom spectrum is referred to the starting surface of pure silicon. It clearly demonstrates the doublet structure of this line as well as some features characteristic of the reconstructed Si(100) $2 \times 1$  surface [12, 13]. Manganese deposition on silicon leads not only to usual damping of the line of Si  $2p$  electrons but also to its considerable energy shift towards lower binding energies as well as to the variation in the line shape itself. It should be emphasized that all these variation occur in a rather broad range of coverages (approximately to  $13 \text{ \AA}$  Mn). Such behavior of the line under consideration indicates a high reaction ability of the system under study and the formation of manganese silicides or other phases with the participation of Si and Mn atoms in the interface region.

The made conclusion is also confirmed by the analysis of the spectra of  $3p$  electrons of manganese measured at various formation stages of the film (Fig. 2). Since this line is a multiplet being character-



**Fig. 3.** Valence electron spectra measured for various deposition doses of manganese on silicon (black curves) and results of their modeling (gray curves).

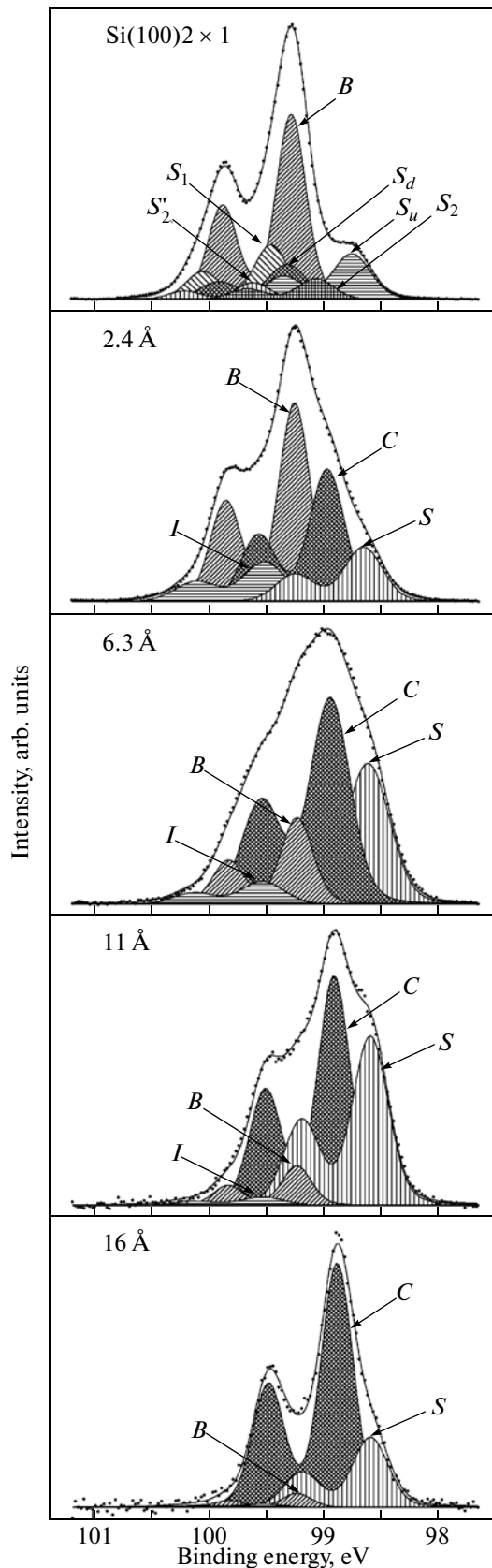
ized by a considerably larger width than the Si  $2p$  line by virtue of this fact, the variation in its shape and location is not as noticeable as in the case of the data of Fig. 1. Nevertheless, it is seen from Fig. 2 that as the coverage grows, a systematic shift of the maximum of Mn  $3p$  electrons towards lower energies is observed. When going from 2.4 to 21 Å Mn, this shift, which reflects the variation of the state of manganese atoms in the analyzed near-surface layer, is equal to 0.3 eV.

Let us now consider the valence electron spectra (Fig. 3). It is seen that they are also sensitive to deposition of manganese. Deposition of the film with the effective thickness of 2.4 Å Mn leads to an abrupt increase in emission of electrons excited from the states near the Fermi level, which indicates an essential increase in the density of electron states in this energy region. Emission of valence-band electrons in the energy region up to  $\sim 3$  eV also noticeably increases in this case. The further increase in the deposition dose gradually varies the shape of the spectrum until two broad maxima at energies of 0.6 and 2.6 eV, which are typical of the bulk manganese sample, start to dominate in it. Thus, the dynamics of the variation in

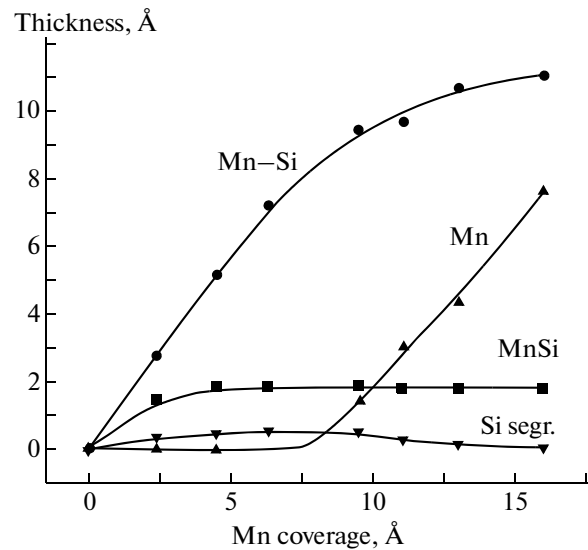
the valence band spectra also indicates that the manganese–silicon phase interface is not atomically sharp and the formation of the interfacial layer precedes the growth of the pure manganese film in this system.

A more detailed information on the formation of the interface under consideration can be found performing the quantitative analysis of the entire totality of measured spectra. Such approach was previously used successfully when studying the Co/Si system [14, 15]. In this case, the Si  $2p$  spectra turn out most informative. Their analysis makes it possible to reveal the phases forming during the interface formation [16]. The decomposition of measured Si  $2p$  spectra into elemental components was performed using the standard procedure described, for example, in [17]. The results of applying this procedure are illustrated in Fig. 4. For clearness, all analyzed spectra in Fig. 4 are presented with the subtracted background and are normalized to the intensity maximum. The points in the upper part of Fig. 4 show the starting spectrum of pure silicon. It is constituted by a bulk component ( $B$ ) and five surface modes, which are denoted by various kinds of hatching; they are conditioned by the reconstruction of the Si(100) $2 \times 1$  surface [12, 13]. It is known that the latter are the modes of upper and lower dimer atoms ( $S_u$  and  $S_d$ ), the first-layer atoms ( $S_1$ ), and the second-layer atoms ( $S_2$  and  $S_2'$ ). The decomposition of the silicon spectrum into the mentioned components (the solid line) agrees well both with the experiment and with the published data.

Deposition of manganese on the silicon surface immediately leads to disappearance of above-mentioned surface modes. This indicates that there are no longer naked segments of silicon possessing the reconstructed surface on the substrate. New components appear in the spectra instead of surface modes. It should be noted that in order to describe the experimental data acquired at all stages of the interface formation adequately, in addition to the above-mentioned mode  $B$ , it was necessary to introduce into the consideration three additional components. They are denoted in Fig. 4 by letters  $C$ ,  $I$ , and  $S$ , and their bonding energies are 98.97, 99.52, and 98.66 eV, respectively. All these new modes manifested themselves already after the deposition of 2.4 Å Mn on the silicon surface. However, the dynamics of the variation in their intensity with the coverage growth was different. For example, mode  $C$  constantly enhanced with an increase in the deposition dose and became dominant in the spectrum after the deposition of 11 Å Mn; to the contrary, mode  $I$  damped rather rapidly, while the dependence of intensity of mode  $S$  on the coverage thickness was peaked at 9.5 Å Mn. Taking into account our previous results on the formation of the Co/Si and Fe/Si interfaces, this behavior of the spectral components under consideration can be explained if we assume that the first of them ( $C$ ) corresponds to the solid solution of silicon in manganese, the second one



**Fig. 4.** Results of decomposition of the Si  $2p$  electron spectra into elemental components. Various types of hatching denote the spectral modes corresponding to various chemical phases.



**Fig. 5.** Dependences of the average thickness of the layers of various chemical phases formed in the region of the Mn/Si interface on the coverage.

(*I*) corresponds to the interfacial manganese monosilicide, and the third one (*S*) corresponds to silicon segregated on the surface of the mentioned solid solution. The comparison of the corresponding bonding energies of Si  $2p$  electrons also indicates in favor of this interpretation. Indeed, the shift of mode *C* to energies lower compared with mode *I* is caused by the enhancement of the role of relaxation processes in the solid solution of silicon in manganese, which is more metallized compared with MnSi. As for mode *S*, which is characterized by the largest negative energy shift of  $-0.6$  eV relative to mode *B*, such a large value is typical of the segregated silicon [16, 18]. The effect of the excess accumulation of silicon on the surface of metals as well as of their silicides was observed in some studies; it is explained by the lower surface energy of silicon compared with metals [19–21].

Finally, it should be noted that the made conclusion on the formation of a thin layer of interfacial manganese silicide and the silicon solid solution in manganese on the Si(100) $2 \times 1$  surface agrees with data [3]. The authors of [3] performed the experiment similar to our experiment, which included the deposition of 1.2 Mn monolayers on the silicon surface.

Based on the experimental dependences of intensity of all modes of Si  $2p$  spectra on the coverage and the assumption on the exponential damping of the signal with an increase in depth, we evaluated the thicknesses of the layers of interfacial silicide, the solid solution of manganese in silicon, and segregated silicon on various deposition doses of Mn. These results are presented in Fig. 5. It turned out that a thin silicide layer Mn/Si is rapidly formed at the early formation stage of the MnSi interface; its effective thickness ( $1.8$  Å) remains invariable for coverages thicker than

