Influence of the Si(111)-2×2-Fe surface reconstruction on formation, morphology and optical properties of manganese silicide

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Abstract

Growth of Mn silicide on the 2×2-Fe and 7×7-Si phases at 400 °C was studied with differential reflection, electron energy losses and Auger electron spectroscopies. Formation of semiconducting Mn silicide (MnSi 1.74) was found, when Mn atoms were deposited on the 2×2-Fe phase. Bandgap of this film is narrower than that of MnSi 1.74 grown on Si substrate by 0.08 eV.

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1. Introduction

Higher manganese silicide (HMS) MnSi 1.74 is a semiconductor, having bandgap from 0.4 to 0.9 eV by different data [1-3]. The silicide thin films, grown on Si(111) substrate, have a high Seebeck coefficient [4,5]. Therefore it is a perspective material for infrared (IR) photodetectors and Peltier cooling system. HMS has a tetragonal crystalline structure with lattice constant of \( a = 0.553 \) nm and unusually long \( c \)-axis up to 10 nm. The unusual crystalline structure of MnSi 1.74 complicates growth of high quality films on
highly symmetric Si substrates [6-9]. To improve quality of HMS film, Mn atoms were deposited on Sb and Bi phases [7,10]. However, during MnSi$_{1.74}$ formation Sb and Bi atoms were defusing into the silicide lattice and as a result Seebeck coefficient was reduced [4]. On the other hand embedding iron atoms in the HMS increased the Seebeck coefficient [4], and so HMS growth on Fe phases could result in improving the crystalline quality and thermoelectric properties of the silicide film. However, MnSi$_{1.74}$ formation on Fe phases was not studied yet. The 2×2 iron silicide phase (FeSi-2×2) has a very smooth surface, so it would be a good template to grow flat HMS films. Therefore the aim of this paper is investigation of the Mn silicide growth on FeSi-2×2.

2. Experiments

All experiments were carried out in ultrahigh vacuum chamber “Varian” with base pressure $2 \times 10^{-10}$ Tor. The samples were cut from boron doped Si(111) wafer with resistivity 45 Ohm·cm. To clean its surface the sample was flash annealed at $T=1250$ °C. To grow the FeSi-2×2 phase, Fe atoms were deposited on cleaned substrate at RT and then the substrate was annealed at 400 °C. Deposition rate was 0.04 nm/min and the Fe film thickness was 0.4 nm. Mn atoms were deposited on the FeSi-2×2 phase and clean Si(111) surface with 7×7 reconstruction (Si-7x7) at 400 °C, deposition rate was 0.13 nm/min. The Mn film thickness was 15 nm. Film composition was in situ investigated with Auger electron spectroscopy (AES) and Electron energy losses spectroscopy (EELS). As-grown samples were studied ex situ with atomic force microscopy and optical spectroscopy. To obtain AES, EELS and IR transmittance reference spectra, a thick MnSi$_{1.74}$ film (488 nm) was grown on Si-7x7 at 400 °C.

3. Results and discussion

The EELS spectrum of Mn film grown on the FeSi-2×2 phase contains bulk plasmon $E_p$ (20.5 eV) and interband transitions (7.0 eV) peaks corresponding to the MnSi$_{1.74}$ (Fig. 1(a)). It means that the formation of the MnSi$_{1.74}$ film occurs. Since bulk plasmon is narrow, the film is crystalline and it does not contain other Mn silicide, e.g. MnSi. There are no Si (17.2 eV) and FeSi-2×2 (10.5 eV) bulk plasmons in the EELS spectrum. It suggests that the silicide film is continuous. This spectrum also contains a bulk plasmon of the surface reconstruction (11.0 eV) forming atop HMS [10]. Since the intensity of the plasmon is high, the area of the surface reconstruction is also high.

![Fig. 1. (a) EELS spectra of clean Si surface (Si-7×7), FeSi-2×2 phase (FeSi-2×2), Mn film deposited on these phases (Mn/Si-7x7 and Mn/FeSi-2×2) and thick MnSi$_{1.74}$ film (bulk MnSi$_{1.74}$); (b) AES spectra of FeSi-2×2 phase (FeSi-2x2), Mn film deposited on this phase (Mn/FeSi-2×2) and thick MnSi$_{1.74}$ film (bulk MnSi$_{1.74}$).](image-url)
Therefore the Mn silicide film is smooth that is confirmed by AFM (Fig. 2(a)). Silicide growth on the FeSi-2x2 phase differs from that on the Si-7x7. In the case Mn atoms deposition on the Si-7x7 phase the MnSi1.74 and metallic MnSi are formed [6]. Therefore a width of the bulk plasmon peak increases and it shifts to low energy, because MnSi bulk plasmon energy is lower than that of MnSi1.74 (see Fig. 1(a)). According to AFM data, the film is rough (Fig. 2(b)). Increasing deposited Mn film thickness results in growth of polycrystalline MnSi1.74 film.

The shape of Mn auger peaks in AES spectrum of the Mn silicide film grown on the FeSi-2x2 corresponds to the MnSi1.74, but small Fe Auger peaks are also observed (Fig. 1(b)). Since the Mn silicide film thickness (42 nm) is higher than an escape depth of Fe auger electrons (1 nm), auger signal contains information about the amount of Fe atoms in subsurface layer of the Mn silicide. It means that Fe atoms segregate when the Mn silicide film is growing on the FeSi-2x2 phase. These atoms can embed in the Mn silicide lattice resulting in strain of the silicide film or the ternary silicide formation. If this ternary silicide were metal, the transmittance in far IR region should be low. The semiconducting ternary silicide would produce special absorption lines. However, the transmittance of the film was high and we did not find any special absorption lines in far IR region. Therefore we supposed that the ternary silicide were not formed.

The optical transmittance in the IR region of the MnSi1.74 film grown on the FeSi-2x2 phase is higher than that of Mn silicide film grown on the Si(111)-7x7 (Fig. 3(a)). The transmittance difference increases in photon energy range of 0.7-1.1 eV with decreasing photon energy. It corresponds to additional metallic...
absorption observed in the film grown on the Si(111)-7×7 and caused by the metallic MnSi silicide. When this metallic silicide absorbs a photon, it does not lead to an electron-hole pair generation but only reduces light intensity. The film grown on the FeSi-2×2 phase does not contain MnSi, so it could be a good material for IR photodetectors.

Absorption coefficient $\alpha$ was calculated for Mn/FeSi-2×2 from the transmittance spectra of bulk Si and Mn/FeSi-2×2 using formula presented in [11]. To find energies of the first indirect and direct transitions, the square root and square dependencies of the production of absorption coefficient $\alpha$ and thickness $d$ of the MnSi$_{1.74}$ film grown on the FeSi-2×2 phase were plotted (Fig. 3(b)). Energy of the first indirect transition, i.e. bandgap of the MnSi$_{1.74}$, is 0.32 eV. It is 0.08 eV lower than bandgap of the MnSi$_{1.74}$ grown on Si [12]. Decreasing bandgap of the MnSi$_{1.74}$ we found results from strain of the Mn silicide lattice when Fe atoms are embedded.

4. Conclusions

When Mn atoms are deposited on the FeSi-2×2 phase at 400 °C only semiconducting silicide MnSi$_{1.74}$ film grows without any metallic MnSi fraction. During the MnSi$_{1.74}$ film formation Fe atoms diffuse into the Mn silicide lattice. It results in strained Mn silicide film growth, so bandgap of the MnSi$_{1.74}$ decreases.

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