Influence of Si(111)-$\sqrt{3}$x$\sqrt{3}$-R30°-Sb surface phase on the formation and conductance of low-dimensional magnesium silicide layer on Si(111) substrate

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Abstract
Using electron energy loss spectroscopy, Raman spectroscopy, and conductance measurements in the temperature range 20–500 K we have investigated doping of two-dimensional Mg silicide using the Sb surface phase. The doping process was performed in two steps including formation of the Sb surface phase followed by reactive deposition of Mg. It was shown that additional levels appear in the Mg$_2$Si band gap resulting in increasing conductance at high temperatures. The Sb doped Mg$_2$Si layer has a band gap of about 1.2 eV.
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1. Introduction
Recently, thermoelectric materials based on Mg$_x$X (X = Si, Ge, Sn) compounds have been intensively investigated because of their promising application in power generation [1]. Highly efficient Mg$_2$Si with Sn and Sb bulk alloys with ZT > 1 have been obtained using various techniques like simple direct melting or sophisticated spark plasma sintering [3]. On the other hand it was reported that nanoscale structural modulation in a Bi$_2$Te$_3$/Sb$_2$Te$_3$ thin film superlattice exhibited ZT values of about 2 [4]. Therefore, in this study we have investigated the growth, structure, and electrical properties of two-dimensional Mg silicide before and after doping using Si(111)-$\sqrt{3}$x$\sqrt{3}$-R30°-Sb surface phase.

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2. Experimental

The growth experiments were performed in two ultrahigh vacuum (UHV) chambers. One of them was equipped with a six-probe unit for electrical measurement [5] and another (VARIAN) with a cylindrical mirror analyzer for Auger electron spectroscopy (AES) and electron energy loss spectroscopy (EELS). In both chambers Mg (99.99%) and Sb (99.99%) sublimation sources and a sublimation source of silicon (boron doped, 1 Ω·cm) were used for growth experiments, including the epitaxial silicon growth atop magnesium silicide layers in certain experiments. Silicon wafers of p-type conductivity 1 Ω·cm with (111) orientation, 4° declination angle, and p-type conductivity 45 Ω·cm with (111) orientation were used as substrates. They were cleaned with organic solvents before loading into the UHV chamber. Then they were outgassed at 650 °C during 8 hours. An atomically-clean surface was obtained after flashes at 1250 °C. The Sb (0.02 nm/min), Mg (0.03 nm/min), and Si (3.0–3.5 nm/min) deposition rates were controlled by a quartz microbalance. Si(111)\(\sqrt{3} \times \sqrt{3}\)-R30°-Sb surface phase (Sb SP) was formed after deposition of one monolayer of Sb on the substrate kept at 650 °C. A two-dimensional magnesium silicide layer was formed by deposition of 1 nm of Mg at room temperature followed by annealing at 150 °C for 5 min or by deposition of 1 nm of Mg on Si substrate at 150 °C. The doping process was performed in two steps. The first one is formation of Sb SP. The second is cooling the sample down to room temperature followed by the growth of 1 nm of magnesium at \(T_{\text{sub}} = 150 \, ^\circ\text{C}\).

Atomic force microscopy (AFM) investigations of samples morphology were performed with a multimode scanning probe microscope Solver P47. Raman spectra of some grown samples were registered with SPM NTEGRA SPECTRA (NT MDT, Russia) at room temperature with a laser (\(\lambda = 488 \, \text{nm}\)) excitation line. Ex situ low temperature measurements of sample resistance were carried out in a cryogen-free cryostat for electrical conductance measurements (RTI Cryomagnetic Systems) with automatically registered current and voltage bias.

3. Results and discussion

Two series of experiments were carried out. The first one is a set of growth experiments with in situ temperature measurements of conductance. Four different samples were investigated: clean Si substrate, Si with Sb SP, Si with undoped Mg silicide, and magnesium silicide grown on a preliminarily formed Sb surface phase (further denoted as “doped”). Almost the same set of samples was grown in the VARIAN chamber with control of AES and EELS spectra. Samples were processed with AFM and low temperature ex situ resistance measurements were made after unloading from the UHV. On the vicinal Si(111) surface a large density of steps and Mg silicide islands were observed. But on the singular Si(111) surface a smaller roughness of grown films was found, which corresponds to the formation of continuous magnesium silicide layers.

![Fig. 1 Logarithm of conductance registered in situ versus reverse temperature of doped and undoped magnesium silicide layer, Sb surface phase, and clean silicon substrate.](image-url)
Let us consider *in situ* temperature measurements of the clean silicon substrate with and without different two-dimensional layers of the Sb surface phase and magnesium silicide. The formation of the Sb surface phase on silicon substrate did not result in an increase in sample conductance at room temperature and a noticeable inclination of conductance dependence compared with bare Si (Fig. 1). Nevertheless a small increase in conductance was observed at higher temperatures. So, we can say that there was only a weak influence of the Sb surface phase on a doping of Si substrate. After the growth of the Mg silicide layer on atomically clean Si substrate the sample conductance and band gap values (1.12 eV) were conserved, which corresponds to the low conductance of the undoped Mg silicide layer. When the Sb surface phase was preliminary formed on Si(111)7×7 surface and then the Mg silicide was grown, increases in the conductance (Fig. 1) and mobility of majority carriers (holes) along with a small increase in the band gap value (1.21 eV) were observed. We can conclude that some doping of the low-dimensional Mg silicide phase occurs after the deposition of Mg at 150°C.

![Raman spectra of Si substrate, doped and undoped Mg silicide layers, and Sb doped thick Mg silicide layer.](image1)

**Fig. 2** Raman spectra of Si substrate, doped and undoped Mg silicide layers, and Sb doped thick Mg silicide layer.

![Temperature dependences of resistance of Si substrate and samples with undoped and doped Mg$_2$Si layers.](image2)

**Fig. 3** Temperature dependences of resistance of Si substrate and samples with undoped and doped Mg$_2$Si layers.
Similar samples together with an additional Mg silicide sample with increased thickness (32 nm) were formed in the second set. According to EELS data, Mg silicide layers grown in experiments have an electronic structure corresponding to two-dimensional Mg\(_2\)Si. The same electronic structure was also observed for thick Mg silicide film. After unloading the samples, the Raman spectra registration (Fig. 2) and low temperature resistance measurements (Fig. 3) were carried out. The formation of the Mg silicide layer is confirmed by the appearance of a well distinguished peak at about 260 cm\(^{-1}\) and a curve bend at 356 cm\(^{-1}\), which are inherent for Mg\(_2\)Si. Their magnitudes strongly increase for the Sb-doped Mg silicide phase, which corresponds to the conservation of the Mg\(_2\)Si structure and ordering after Sb doping. Similar behavior with an additional increase in the 356 cm\(^{-1}\) peak intensity was observed for the thick Mg\(_2\)Si film doped by Sb atoms.

Low temperature measurements of sample resistance in the temperature range of 25–240 K (Fig. 3) have shown that for all samples on Si(111) 4° substrates, including clean silicon substrate, the freezing of free carriers is observed at temperatures less than 40 K. The maximal resistance at temperatures higher than 200 K was observed for clean Si substrate. The decrease in resistance in grown samples is explained by two facts: (1) additional conductance through the two-dimensional Mg\(_2\)Si layer and (2) formation of Sb doping levels in the Si or Mg\(_2\)Si band gap. The undoped Mg\(_2\)Si sample is characterized by carrier freezing at temperatures less than 190 K. But in the doped one the carriers were frozen at 140 K.

4. Conclusions

EELS, Raman spectroscopy, and conductance data have shown that an Mg\(_2\)Si ordered lattice is conserved after growth atop an Si(111)\(\sqrt{3}\times\sqrt{3}-R30^\circ\)-Sb surface phase on vicinal and singular surfaces, and additional doping levels appear in the Mg\(_2\)Si band gap, which results in an increase in conductance at temperatures higher than 140 K. In situ Hall temperature measurements have also shown that the Sb-doped 2D Mg\(_2\)Si layer has a band gap of about 1.2 eV.

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