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Silicon overgrowth atop low-dimensional Mg\textsubscript{2}Si on Si(111): structure, optical and thermoelectrical properties

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Abstract

The growth of silicon cap layers atop Mg\textsubscript{2}Si nanocrystallites (NCs) and Mg\textsubscript{2}Si two-dimensional layer with structure $\sqrt{3} \times \sqrt{3}$-R30\textdegree were studied by methods of AES, EELS, AFM, optical and Raman spectroscopy. It was established that method of solid phase epitaxy (SPE) ensures the embedding of Mg\textsubscript{2}Si NCs in polycrystalline quality silicon cap layer at temperatures not higher than 920 K. The increase of the temperature higher than 970 K results to the moving of silicide NCs toward the surface between silicon grains in cap layer, following their destruction and Mg desorption from the surface. The MBE method with temperatures 430-485 K was used to the embedding of continuous 2D Mg\textsubscript{2}Si layer with structure $\sqrt{3} \times \sqrt{3}$-R30\textdegree in silicon top layer (9-20 nm) with monocrystalline grains. Investigations of thermoelectrical properties of grown nanoheterostructures have shown that a Seebeck coefficient ($\alpha \approx -130 \mu V/K$) increases in ten times as compared with undoped silicon substrate ($\alpha = 10 - 15 \mu V/K$).

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1. Introduction

The magnesium silicide (Mg\textsubscript{2}Si) has similar to Si, a cubic structure with a larger lattice parameter. The lattice mismatch of Mg\textsubscript{2}Si(111) plane with Si(111) plane is 1.9% [1]. The high quality epitaxial growth of Mg\textsubscript{2}Si(111) on Si(111) substrate is possible due to the comparatively small lattice mismatch [2]. However, the thin film formation is complicated by the low condensation and high vapor pressure of Mg that is why a thin Mg\textsubscript{2}Si film preparation and properties studies are scarce.

The formation of low-dimensional Mg\textsubscript{2}Si in the form of islands and thin layers on and in silicon substrates is interesting for creation of silicon-based materials with new photoelectric and thermoelectric properties. The formation of ordered two-dimensional magnesium silicide phase with $\sqrt{3} \times \sqrt{3}$-R30\textdegree structure [1] and nanosize...
Mg$_2$Si islands [3] on Si(111) have been early observed. However, the silicon epitaxial growth atop low-dimensional Mg$_2$Si and thermoelectrical properties of this nanoheterostructures is unknown today.

2. Experiments

Growth experiments were carried out in ultra high vacuum (UHV) chamber (with base pressure of 2.10$^{-10}$ Torr) equipped with AES spectrometer, sublimation sources of Si and Mg and quartz sensors of film thickness. Si(111) wafers with 1-45 $\Omega$ cm resistivity were used as substrates for different series of growth experiments. For growth of nanosize Mg$_2$Si silicide islands the small Mg thickness (1.0 nm) was deposited on silicon surface and then annealed at 650 K. Silicon overgrowth (90-50 nm) with deposition rate of 1-1.5 nm/min was carried out by solid phase epitaxy (SPE) at 820–1020 K. For the formation of Mg$_2$Si phase with structure ($\sqrt{3} \times \sqrt{3} \times \sqrt{3}$)-R30$^\circ$ the small Mg thickness ($d$=1 nm, $V_{Mg}$=0.5 nm/min) was deposited on silicon and then annealed at 420 K during 5 minutes. Silicon overgrowth (9-85 nm) with deposition rate of 0.17 nm/min was carried out by molecular beam epitaxy (MBE) at 420 K. Some samples had an additional annealing at 820 K (t=20 min) and 870 K (t=10 min) after MBE Si growth. Different properties like sample morphology, optical and Raman spectroscopy, and thermoelectricity were investigated on the samples with embedded Mg$_2$Si nanocrystallites (NCs) and 2D Mg$_2$Si layers after its unloading from UHV chamber.

3. Results and Discussion

The AFM topography pictures of the Si(111)/NCs Mg$_2$Si/Si samples grown by SPE method at 770-1020 K have shown, that samples surface consist of granules with sizes from 50 to 500 nm. It was observed that with increase of annealing temperatures the substrate roughness was decreased (from 9.1 to 3.2 nm), that should be consequence of improving of Si layer crystal quality. However, an additional contribution at 2.1-2.3 eV was observed in the reflectance spectra at increasing of annealing temperature ($T_{ann}$). Mg$_2$Si islands were closer to surface in a sample annealed at 920 K than in sample with smaller annealing temperature (820 K). Therefore, the decrease of surface roughness with increasing of $T_{ann}$ can be explained by moving of silicide islands to the surface between silicon grains in cap layer and Mg desorption from it on the surface. This assumption has been proved by far infrared spectroscopy data [4]: at $T_{ann}$=820 K the Mg$_2$Si islands are still inside silicon, at $T_{ann}$=970 K – the islands move to the surface and at $T_{ann}$=1020 K – all silicide islands quickly destroy inside silicon, Mg atoms diffuse to the surface and desorb from Si surface, since the Mg$_2$Si phonon peaks in far infrared spectra are absent.

By AFM data the surface of the sample after silicon MBE ($T$=420 K, 20 nm) overgrowth atop 2D Mg$_2$Si with structure ($\sqrt{3} \times \sqrt{3} \times \sqrt{3}$)-R30$^\circ$ is covered by granules with sizes 70-100 nm, height 5-9 nm and density 1x10$^{10}$ cm$^{-2}$. The surface roughness equals 6 nm. Thus, granules gather in conglomerates till 15-20 pieces, between which smooth areas with sizes from 100 up to 1000 nm are observed. Additional annealing at 820 K during 20 minutes results in decrease of roughness down to 3.0 nm and granules have the same sizes, but less height (2-4 nm). However, after annealing the size of areas between conglomerates decrease to 70-300 nm, i.e. the granules practically uniform cover all sample surface. The increase of additional temperature annealing up to 870 K during 10 minutes results in significant changes of sample relief (roughness – 9.9 nm). So, an advanced surface, probably, is consequence of Mg$_2$Si destruction and migration to the surface that should result in re-crystallization of the underlying silicon layer at this temperature. The surface of the sample after silicon MBE ($T$=420 K, 85 nm) consists of flat triangle regions of different heights by AFM data, that correspond to the formation of silicon with good crystalline quality atop magnesium silicide with structure ($\sqrt{3} \times \sqrt{3} \times \sqrt{3}$)-R30$^\circ$.

From Raman-spectra (Fig. 1) it is seen that samples, which were grown by MBE technology, are characterized by position and form of monocristalline Si Raman-peaks. An additional shoulder around the main Si Raman peak (520 cm$^{-1}$) is observed in the field of 470-500 cm$^{-1}$ for the sample, which was grown by SPE technology at $T_{ann}$=820 K. Peak broadening in the field of smaller Raman shifts testifies to the crystal quality degradation of silicon layer. The shoulder in the range of 490-500 cm$^{-1}$ testifies to the polycristalline character of film, but not to an amorphous one (for amorphous Si at 450-470 cm$^{-1}$ (Fig. 1)). The sample with 9 nm of Si top layer thickness, which was grown by MBE technology, has two additional high intensity peaks at 256 and 345 cm$^{-1}$ in Raman spectrum (Fig. 1). These peaks correspond to magnesium silicide phonons [5], which testify to the presence of Mg$_2$Si inside silicon and to a good crystalline quality of it. The absence of these peaks for sample with 20 nm silicon
thickness (for MBE growth) is caused by the limited penetration depth of laser radiation in silicon (about 15 nm) and impossibility of output and registration of Raman signals at given and greater thickness of silicon.

After reloading of grown sample from UHV chamber the measurements of thermoelectrical properties were done in the temperature range of 330-470 K. The temperature dependences of Seebeck coefficient for p-type silicon with 45 Ω•cm resistivity (plates from this silicon have been used as samples substrates) and four samples, prepared by SPE and MBE technology, are presented on Fig. 2. It is seen that silicon substrate has the maximal values of Seebeck coefficient at 22 μV/K (330 K) and -10 μV/K (460 K). The change of Seebeck coefficient sign at increased temperature (435 K) is caused by increase of the electron contribution in total thermoelectricity due to generation of electron-hole pairs at the transition to intrinsic conductivity area, because the electron mobility in silicon is more than the hole mobility.

The sample with two layers of Mg2Si NCs (Fig. 2, 2L) is characterized by bigger values of Seebeck coefficient (53 μV/K and -130 μV/K) in comparison with a substrate. It’s caused by generation of carriers in Mg2Si NCs and their injections in silicon substrate. It has been early shown [6] that the potential barrier in Mg2Si/Si heterojunction for electrons is lesser, than one for holes. Hence, the significant growth of Seebeck coefficient at temperatures bigger 420 K is caused by generation of carriers in Mg2Si NCs and only electrons from Mg2Si NCs inject in a silicon layer across Mg2Si-p/Si-p heterojunction. Reducing of the maximal values of Seebeck coefficient (36 μV/K and -87 μV/K) with increasing of quantity of layers of Mg2Si NCs (Fig. 2, 4L) was observed. The increase of quantity of buried Mg2Si NCs layers causes the degradation of crystal quality of cap silicon layers that is confirmed by optical spectroscopy and Raman spectroscopy data.

The sample with buried 2D Mg2Si layer, prepared by MBE technology (Fig. 2, 20 nm), is characterized by the maximal values of Seebeck coefficient at 130 μV/K and -47 μV/K. The bigger maximal value of Seebeck coefficient is caused by larger concentration of charge carriers (holes) in 2D Mg2Si in comparison with Mg2Si NCs and also by the best crystal quality of a cap silicon layer (according to Raman spectra).
Increasing of Seebeck coefficient with increasing of temperature (in range of 330-420 $\degree$C) is caused by generation of carriers (holes) in magnesium silicide and injection it’s to silicon layer. A generation of electron-hole pairs (in silicon and Mg$_2$Si) at the transition to intrinsic conductivity area is occur at temperatures higher 400 $\degree$K that results to decreasing of Seebeck coefficient and changes of it sign. The increase of cap layer thickness up to 85 nm results in reduction of influence of 2D Mg$_2$Si layer on the total system thermoelectricity. 

Thus, the Si/Mg$_2$Si/Si(111) heterostructures with embedded 2D Mg$_2$Si with structure ($\sqrt{3}x\sqrt{3}$)-$R30^\circ$ is more preferable for the creation of thermal converter, because they has bigger values of Seebeck coefficient in comparison with Si/Mg$_2$Si/Si(111) heterostructures with Mg$_2$Si NCs.

4. Conclusions

Silicon cap layers grown atop Mg$_2$Si nanocrystallites (NCs) and Mg$_2$Si two-dimensional layer with structure ($\sqrt{3}x\sqrt{3}$)-$R30^\circ$ by SPE and MBE methods were studied by AES, EELS, AFM and Raman spectroscopy. It was found that Mg$_2$Si NCs are embedded in polycrystalline quality silicon cap layer during SPE growth method at temperatures not higher than 920 K. But the increase of annealing temperature up to 970 K results to the moving of silicide NCs toward the surface between silicon grains in cap layer and Mg desorption from it on the surface. It was observed that annealing temperature $T_{ann}=1020$ K is high enough, such that silicide NCs quickly destroy inside silicon, following Mg atoms diffusion to the surface and desorb from it.

Unlike to SPE method the MBE method with temperatures 430-485 K results to the formation of Si monocrystalline grains in top layer with thicknesses (9-20 nm), in which the 2D Mg$_2$Si layer is embedded and conserves a continuity. A discrepancy of Si(111) and 2D Mg$_2$Si lattices (1.9 %) opposes to the growth of atomically smooth silicon cap layer surface even at thickness of 85 nm.

Investigations of thermoelectrical properties of grown nanoheterostructures have shown that a Seebeck coefficient increases in tens times as compared with undoped silicon substrate. It was established that Si-p/ Mg$_2$Si NCs/Si(111)-p nanoheterostructures are characterized by smaller values of Seebeck coefficient ($\alpha$=20-30 $\mu$V/K) in comparison with one ($\alpha$=130 $\mu$V/K) of Si-p/2D Mg$_2$Si/Si(111) nanoheterostructures. This fact is caused by smaller quantity of magnesium silicide and the worse crystal quality of a covering silicon layer with embedded Mg$_2$Si NCs.

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References