Multilayer Si(111)/Mg$_2$Si clusters/Si heterostructures: Formation, optical and thermoelectric properties

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The technology of solid phase growth of multilayer structures with buried nanosize magnesium silicide clusters has been developed. Basing on the experimental data, a conclusion was made that magnesium silicide clusters remain in depth of the Si layers at $650^\circ$C and give a contribution in the effective dielectric permeability and effective electron number of multilayer structures. The huge increase of a thermoelectric power coefficient for samples with buried magnesium silicide clusters in comparing with one for the bare p-type silicon substrate has been observed. [DOI: 10.1380/ejssnt.2005.12]

Keywords: Silicon; Magnesium silicide; Solid phase growth; Clusters, Multilayer formation; Optical parameters; Thermoelectric power

I. INTRODUCTION

Magnesium silicide (Mg$_2$Si) as a narrow-gap semiconductor represents certain interest for silicon planar technology. The fundamental electronic properties of magnesium silicide monocrystals have been widely investigated both theoretically, and experimentally [1–5]. First principl principle calculations of energy band structure of Mg$_2$Si monocrystals [1, 4] have been carried out. It has been shown that magnesium silicide is an indirect-gap semiconductor, however the energy band gap differs significantly by calculation data: $E_g = 0.37 \sim 0.7$ eV. The calculations have been satisfactorily coordinated with the optical spectroscopy data ($E_g = 0.60 \sim 0.66$ eV [6]) and temperature measurements of resistivity ($E_g = 0.78$ eV at 0 K [5]). The concentration and mobility of carriers in magnesium silicide monocrystals have been determined: $n = 8 \times 10^{16} \sim 10^{18}$ cm$^{-3}$, $p = 4 \times 10^{17}$ cm$^{-3}$, $\mu_n = 200 \sim 406$ cm$^2$/V·sec, $\mu_p = 56$ cm$^2$/V·sec [5, 7].

Recently serious attention of researchers is concentrated on cluster structures on the basis of silicon [8–10]. The semiconductor materials created on the basis of buried clusters can possess new optical and electric properties, which are important for construction of new kinds of device structures. Formation of cluster structures begins with creation of high-density islands of one semiconductor on the other semiconductor material. However, in a technological process it is necessary to overgrow an epitaxial layer of silicon upon the islands, therefore for each new system it is necessary to find optimum conditions of growth and to investigate the properties of cluster materials obtained. In the multilayer concept [12, 13] an increase of thermoelectric figure of merit ($Z$) can be achieved on the basis of two effects: by quantum confinement in quantum well structure [12] or quantum dot structure and by an enhanced phonon scattering at the interfaces [13]. Silicon with buried magnesium silicide clusters is of interest for creation of new thermoelectric generator modules, because magnesium silicide possesses high thermoelectric power [11], and the quantum dot structure could be formed in this case.

In the present work the formation of Mg$_2$Si islands on Si(111) is studied, the growth technology of Mg$_2$Si cluster layers buried in the bulk silicon is developed and thermoelectric and optical properties and parameters of the electronic structure of the obtained multilayer materials are investigated.

II. EXPERIMENTAL

The experiments on Mg$_2$Si film growth were carried out in the ultrahigh vacuum system ‘VARIAN’ with base pressure $2 \times 10^{-10}$ Torr. The chamber is equipped with an Auger-electron spectrometer, a manipulator with four degrees of freedom, a sample holder for three samples, a block of evaporation sources (Cr, Fe, Mg, Si), a quartz thickness-sensor. It is possible to separately heat each sample with direct current. The current values were pre-calibrated to provide the required temperatures. Silicon (111) wafers of the p-type with resistance of 10 Ω cm and the sizes of $5 \times 18 \times 0.35$ mm$^3$ were used as substrates. Before loading into the vacuum chamber the substrates were chemically cleaned. Atomically clean surface of silicon (Si (111)7×7) was prepared by two-step annealing at $700^\circ$C during 4–5 hours and $1250^\circ$C during 1 minute (in flashing regime by 3–5 seconds with 30–60 seconds intervals). The control of surface cleanliness was carried out...
by Auger electron spectroscopy (AES). Magnesium was evaporated at portions from a Ta-tube heated by direct current. Chemically pure magnesium (99.99%) was used for the Mg source. Magnesium deposition rate varied in the range of 0.05 ∼ 0.5 nm/min. A p-type silicon plate with doping concentration $3 \times 10^{16}$ cm$^{-3}$ and the sizes of $5 \times 18 \times 0.35$ mm$^3$, heated up to the sublimation temperature by alternating current was used for silicon deposition. Composition and electronic structure of the grown samples were investigated by AES and electron energy loss spectroscopy (EELS) methods.

In order to create layers of magnesium silicide islands, one nanometer-thick layers of magnesium were deposited on atomically clean surface Si(111)7×7 at room temperature, and then the sample was annealed at the temperature 380°C for one minute. At this temperature some part of magnesium atoms desorbed from the silicon surface [14], and the rest of them reacted with silicon atoms from the substrate, forming nanosize islands of magnesium silicide. For some samples the islands were buried with a 20 ∼ 50 nanometer-thick layer of silicon and annealed at 650°C. The structures with three buried layers of magnesium silicide islands were grown by the same method and annealed at the temperature 650 or 750°C. Thickness of each silicon layer between the magnesium silicide layers was 10 nanometers, except the top layer of silicon which was 50 nm-thick. Crystallization of silicon layers in the multi-layer structure was carried out after deposition of the top layer of silicon.

The surface topography of as-grown samples was investigated ex-situ with a multimode atomic force microscope (AFM) SOLVER P47 of the company NT-MDT. Two scanning modes were used: the contact and semi-contact modes. In the contact mode of scanning the needle of the cantilever slides on the surface and follows the topography of the sample with maximal resolution. In this mode it is also possible to obtain the image, which characterizes the friction coefficient between the needle and the sample surface (Lateral Force). In the semi-contact mode some RF-voltage is fed to the cantilever that makes the cantilever beam to oscillate at a certain frequency. In this mode the needle periodically knocks the surface, also repeating its contour. Therefore, the semi-contact mode of scanning is gentler, since the hardness of a surface can be comparable or less than the hardness of the needle.

The optical spectral ex-situ measurements were carried out in the energy range of 0.024 ∼ 6.2 eV with automatic computer system on the basis of the monochromator MDR-3 and three spectrophotometers SPECORD 71IR, SPECORD UV-VIS and SPECORD M80. Transmission (T) and reflection (R) spectra were registered in the energy range of 0.1 ∼ 1.25 eV. Additional reflectance spectra were recorded in the energy range of 0.1 ∼ 6.2 eV at room temperature (RT) with the spectrophotome-
ter SPECORD UV-VIS and the monochromator MDR-3. Atom oscillations were studied by transmission spectroscopy in the energy range of 0.024–0.5 eV with the spectrophotometer SPECORD M80. Calculations of the main optical functions of buried Mg$_2$Si nanocluster structures on the Si(111) substrate have been carried out for the transparency region from $R$- and $T$-spectra using the one-layer model [15] with two equally polish surfaces. An Al mirror, whose absolute reflectivity had been measured previously, was used as a reference at near-normal incidence reflectance measurements. Optical functions ($n, k, \epsilon_1, \epsilon_2$) of silicon and silicon nanocluster materials in the energy range of 0.1–6.2 eV were also calculated from the reflectance spectra, using Kramers-Kronig integral relations [15]. Effective number of electrons per elementary cell and effective dielectric function of grown materials were calculated with use of integrated rules of the sums for optical functions [15].

After optical and AFM measurements grown samples were transferred to the low vacuum cell ($P = 2 \times 10^{-2}$ Torr), where $ex$ $situ$ thermoelectric temperature measurements were carried out within temperature range of 30–150°C. The sample temperature during the measurements was controlled by thin copper-constantan thermocouples, mounted inside the copper plate with two small electrical heaters, which ensured the sample heating and temperature gradient (5–10°C). Two tungsten probes, placing straight over the thermocouples, pressed the sample to the copper plate. The sample was isolated from the plate by thin mica layer. The thermoelectric energy was measured by means of tungsten probes. Thermoelectric power coefficient was calculated from measured thermoelectric power and temperature gradient at each average measured temperature.

### III. RESULTS AND DISCUSSION

By deposition of 1 nanometer of magnesium on atomically-clean silicon surface and annealing of the sample at 380°C the Mg$_2$Si islands with 60–80 nm sizes and the density $(1.5 \sim 2.0) \times 10^9$ cm$^{-2}$ (Fig. 1(a)) were formed on the silicon surface. Root-mean square roughness (RMS-value) of the sample did not exceed 3 nm. As shown in Fig. 1(b), the sample surface is basically homogeneous, i.e. it consists of one substance - silicon, but there are some nanosize islands of other substance - magnesium silicide on it. Formation of magnesium silicide islands was proved by AES and EELS data [16]. For formation of magnesium silicide the silicon atoms were taken from the substrate, thus, the regions adjacent to the clusters were subject to erosion; that correlates with data of STM study of Si(100)-Mg system [17]. It is well seen from the AFM picture cross-section (Figs. 1(c)(d)) that a hollow with depth of 2–5 nanometers and width of 30–50 nm exists around every island; that proves the mechanism of surface silicon diffusion on the borders of islands at low annealing temperature.

As seen from Fig. 2(a), the topography of the sample surface became rougher after deposition of the silicon layer (thickness 50 nm) over the sample with nanosize islands of magnesium silicide. Absence of facets on silicon grains evidences that the polycrystalline silicon film was formed at deposition and annealing of silicon, and the temperature 650°C is not sufficiently high for full re-crystallization of the silicon layer atop the magnesium silicide clusters. AFM data (Lateral force, Fig 2(b)) confirmed, that magnesium silicide clusters are covered with homogeneous silicon film without segregation of magnesium silicide on the surface. The film consists of grains with the sizes of 50–100 nm with RMS-value of about 12 nanometers. The increase of RMS-value as compared with Mg$_2$Si islands on Si also proves a 3D mechanism of silicon growth.

Researches of the morphology of samples with three buried layers of magnesium silicide clusters on silicon show (Fig. 3(c)), that for annealing temperature $T = 650$°C the sample topography represents a set of grains of the rectangular shape with the sizes $150 \times 200$ nm$^2$. Grains have two different directions of growth, perpendicular to each other. Smaller grains have the form close to a square or oval. In spite of the fact that the grains were formed on Mg$_2$Si islands a mean square-root roughness is only 6.82 nm. It was supposed, that increase of the annealing temperature would yield a smoother surface of the sample. However, after annealing at the temperature $T = 750$°C (Fig. 3(d)) the grains had the sizes of $120 \times 120$ nm$^2$ and sphere-like shape. The root-mean square roughness for

**FIG. 2:** AFM data for one-layer buried structure: (a) Contact mode, (b) Lateral force mode, (c) statistical distribution of roughness for the sample with buried cluster structure grown at 650°C.
this sample was 16.2 nm. Consequently, the increase of the annealing temperature results in rougher relief of the sample surface, but does not provide crystallization of the deposited silicon layers. So the increase of the annealing temperature leads to increase of the bulk silicon diffusion and could destroy cluster layers in silicon matrix. Only the longer annealing time at fixed temperature (650°C) could support the crystallization process in silicon cap layer.

The roughness generally depends on the size of the scanning area [18]. Root-mean-square roughness ($\sigma_{\text{rms}}$) has been measured as function of the scanning area length ($L$) in the plane of sample surface for all grown samples. These measurements were carried out by AFM method in the semi-contact mode. The length of the scanning area varied in the range 0.2~16 $\mu$m. As seen from Fig. 4, for all samples $\log(\sigma_{\text{rms}})$ varies linearly with $\log(L)$ before saturation; that is typical for the self-affine growth mode [19], i.e. $\sigma_{\text{rms}} \sim L^h$. The value $h \approx 1$ is consistent with atomistic model of 3D island growth, implying extensive surface diffusion [20] as, for example Si and Mg in the case of Mg$_2$Si film growth ($h = 1.025$) [18] on silicon substrate. When the $'h'$-value varies in the range of 0.3~0.5 only the limited lateral diffusion [18] must be observed. By our data the $'h'$-values are smaller than unity (Fig. 4) for all grown samples. The minimal $'h'$-value has been observed for sample with three buried cluster layers ($h = 0.459$, $T = 650^\circ$C), and the maximal one ($h = 0.872$) has been observed in three-layer samples grown at 750°C. In both case such behavior corresponds to decrease of diffusion transfer of magnesium in samples in comparison to the thick magnesium silicide films. In saturation region the three-layer sample with annealing temperature $T = 650^\circ$C has smoother surface relief (smaller RMS-value) in comparison with the single-layer sample and three-layer sample with annealing temperature $T = 750^\circ$C, that corresponds to silicon surface smoothing and full burying of magnesium silicide clusters in silicon. So we can assume, that the density and distribution of clusters in the three-layer sample grown at 650°C remains the same as before the annealing. For a three-layer sample with annealing temperature $T = 750^\circ$C the exponent factor in the $\sigma(L)$ dependence is 0.872, that corresponds to some increase of diffusion transfer of magnesium. So the diffusion transfer of magnesium increases with increase of the annealing temperature that does not allow suggesting a stability of the system with three cluster layers inside the silicon matrix.

Reflection spectra from the clean silicon substrate, magnesium silicide film and samples with buried cluster structures are presented in Fig. 5. Our previous data on optical spectra of a thick magnesium silicide film have been taken for comparison [16]. From the spectra it is seen, that both for three-layer and single-layer structures some typical features are observed. First of all the decrease of reflection coefficient in all energy range used is

FIG. 3: AFM data (contact and lateral force modes) for three-layer buried structure formed at 650°C (a, c) and at 750°C (b, d).

Rms = 6.82 nm

Rms = 16.2 nm
observed. Only for one-layer sample an additional contribution in the reflectance spectrum is discerned in the energy range of 1.0∼2.5 eV, but for three-layer samples it is weakly distinguishable. For reflectance spectra of samples with buried Mg$_2$Si clusters the small shifts (smaller than 0.1 eV) of silicon 3.4 eV and 4.5 eV peaks [21] are observed towards higher and smaller energies, respectively. Peaks of silicon in buried cluster structures become wider and shift to the lower energy with increase of the annealing temperature (for three-layer structures) and to higher energy for single-layered structure. Such a behavior could be explained by the changes of interband transition probabilities in polycrystalline silicon cap layer near the Mg$_2$Si/Si interface, where the tensions in silicon lattice could be expected.

Calculations based on Kramers-Kronig integral relations have shown (Figs. 6(a)(b)), that dielectric function ($\varepsilon = \varepsilon_1 + i \varepsilon_2$) of silicon with buried Mg$_2$Si clusters (in one-layer and three-layer structures) is mainly determined by the polycrystalline nature of a covering silicon film and Mg$_2$Si clusters. The contribution of Mg$_2$Si buried clusters is maximal at energy 0.1∼2.5 eV, when the silicon top layer is transparent for incidence light [21]. It is very similar to the contribution of polycrystalline Mg$_2$Si film grown at 420°C [16]. So the defects on hetero-interface Mg$_2$Si/Si determine the value of absorption coefficient, since for epitaxial Mg$_2$Si film [16] its value is a small one in this photon energy range. Only peak of imaginary part of dielectric function at 2.0 eV for one-layer structure (Fig. 6(b)) could be related to Mg$_2$Si contribution, since the
silicon top layer thickness (20 nm) is small to full light absorbance. The contribution of Mg$_2$Si clusters is weaker visible below 2.5 eV in three-layer structures, since the silicon top layer thickness (50 nm) is enough for nearly full absorbance of incident light at these energies. Small values of $\varepsilon_1$ and $\varepsilon_2$ at energy 2.5~6.2 eV are determined by the polycrystalline nature [15] of the silicon film situated atop Mg$_2$Si clusters. The polycrystalline silicon layer also makes the main contribution to the dielectric function of samples (and absorption coefficient spectrum) with three buried magnesium silicide cluster layers in silicon at energies higher than 3.0 eV. At elevated annealing temperature (750°C) the high-energy (3.4 and 4.5 eV) peak contribution in dielectric function increases, so the crystalline quality of silicon top layer also increases.

Calculation of $\varepsilon_{\text{eff}}$ for the grown samples (Fig. 7(a)) has shown, that at 6.2 eV energy the dielectric function of the magnesium silicide film is $\varepsilon_{\text{eff}} = 14.7$, and for the silicon monocrystal $\varepsilon_{\text{eff}} = 10.8$. In the case of sample with one buried Mg$_2$Si cluster layer the $\varepsilon_{\text{eff}}$ value at 6.2 eV is smaller than that for silicon. But the contribution of transitions from defect energy levels on Mg$_2$Si/Si interface results in faster increase of $\varepsilon_{\text{eff}}$ in the energy range of 0.1~2.0 eV as compared with Si and magnesium silicide epitaxial film. The increase of the number of buried cluster layers up to three results in increase of $\varepsilon_{\text{eff}}$ (up to 13.0~14.5) at 0.1~6.2 eV that corresponds to increase of the contribution from transitions in three layers of magnesium silicide clusters and defect energy levels on Mg$_2$Si/Si interface in the electronic structure of grown layers.

Calculation of the effective number of electrons per a unit cell has shown (see Fig. 7(b), that in Mg$_2$Si film the $n_{\text{eff}}$ is close to 8.5 electrons per a unit cell. For samples with one buried layer of clusters the $n_{\text{eff}}$ value does not exceed 1.5 electrons per a unit cell, and in samples with three layers of clusters - it increases up to 1.8~2.4 electrons per a unit cell. It is known that in the energy range up to 6 eV less than 4 electrons on unit cell could be observed in monocrystalline silicon [15]. Since in our case only polycrystalline silicon cap layers have been grown in one-layer samples, so the effective number of electrons contributed from silicon layers must be decreased. The increase of annealing temperature in three-layer sample has led to increase of $n_{\text{eff}}$ value that corresponds to the some crystallization of silicon cap layer. Partial contribution of electrons per a unit cell from Mg$_2$Si clusters has been observed in the energy range of 0.5~2.5 eV, where the silicon cap layer is else transparent for one-layer and three-layer samples. So the effective electron number at maximal photon energies (3.0~6.2 eV) determines the silicon contribution in the electron structure of grown materials, but the effective number at small photon energies...
FIG. 8: Transmittance spectra in the range of wave numbers 300∼800 cm$^{-1}$ of the silicon, Mg$_2$Si film and samples with buried clusters. In order to make the transmittance spectra better distinguished from each other, additional shift by $T = 0.15$ was inserted with respect to the previous spectrum.

(0.5−2.5 eV) we can characterize by the contribution of magnesium silicide clusters and defect energy levels on Mg$_2$Si/Si interface.

For one-layer and three-layer samples the transmittance spectra (Fig. 8) have been recorded in the range of wave numbers 300∼800 cm$^{-1}$. All transmittance spectra of the samples were compared with the tabulated data for monocrystal silicon [21]. An absorbance at wave number range 420∼430 cm$^{-1}$ is observed for the one-layer sample grown at 650°C. This peak corresponds to the absorption with the longitudinal optical phonon in magnesium silicide [11]. The resolution of this peak in cluster materials with small quantity of magnesium silicide, in comparison with the thick magnesium silicide film, testifies the high sensitivity of far IR spectroscopy. But in three-layer sample this peak shifts to smaller number value (400∼410 cm$^{-1}$) corresponding to silicon longitudinal optical phonon [15]. Hence, we guess that the crystal structure of the Mg$_2$Si clusters really preserves in silicon matrix at growth temperature of 650°C. But the temperature of 750°C evidently is high for the preservation of Mg$_2$Si clusters in silicon matrix, since it is higher than the melting temperature of bulk Mg$_2$Si [11]. So at this temperature destruction of buried Mg$_2$Si clusters can take place inside the silicon matrix and evaporation from the free surface of the holes observed on the sample surface (Fig. 3(b)).

On Fig. 9 temperature dependencies of thermoelectric power coefficient for bare silicon substrate, magnesium silicide epitaxial film, one-layer and three-layer cluster samples, grown at different temperatures, are presented. In silicon the value of thermoelectric power coefficient was positive and very small (2−5 $\mu$V/K) at temperatures higher 340 K. It is seen that thermoelectric power coefficient for Mg$_2$Si film (−(20 ∼ 70) $\mu$V/K), grown on p-type silicon substrate, has the negative sign that corresponds to electron as majority carriers in the film. However, for samples with buried Mg$_2$Si clusters a thermoelectric power coefficient value was strongly increased in absolute value up to −(160 ∼ 360) $\mu$V/K. The maximal absolute value corresponds to the one-layer and three-layer samples grown at 650°C. When the annealing temperature was increased up to 750°C a thermoelectric power coefficient value decreased in absolute value; that correlates, by far IR spectroscopy data (Fig. 8), with partial Mg$_2$Si cluster destruction.

Since a thermoelectric power coefficient (Fig. 9) is higher than for p-type silicon and Mg$_2$Si film, so the part of Mg$_2$Si clusters preserves inside silicon matrix. What is the reason of such huge increase (in 50∼180 times) of the thermoelectric power coefficient in buried cluster samples in comparing with the bare p-type silicon. We cannot answer on this question now. It is known [22] that thermoelectric power is determined by the Fermi level position and carrier concentration in semiconductors. Since in Mg$_2$Si grown by layer-by-layer procedure electrons are majority carriers, buried Mg$_2$Si clusters inject in p-type silicon matrix free electrons with concentration larger than the hole concentration in silicon. The reasons of such injection could be understand only after detailed investigation of thermopower in the temperature range (77∼500 K) and photoelectric measurements for design of energy band structure of Mg$_2$Si-n(nanoclusters) /Si- p heterojunction. The contribution of enhanced phonon scattering at the Mg$_2$Si cluster/Si interface on the electron injection process could be taken into consideration, too.
IV. CONCLUSIONS

Formation of nanosize islands of magnesium silicide on Si (111)7x7 in the process of solid-phase growth at \( T = 380^\circ \text{C} \) has been investigated. It was established, that three-dimensional islands with narrow distributions of size (60~80 nanometers), height (5~12 nm) and density (up to \( 2 \times 10^9 \text{ cm}^{-2} \)) are formed on Si(111) substrate. From the AES, EELS and AFM data for solid-phase growth of silicon on magnesium silicide islands their segregation on the silicon surface has not been observed. The technique of solid-phase growth of three-layer structures with buried magnesium silicide clusters has been developed. Smoothing of the sample surface during growth process has been shown. The phonon structure of magnesium silicide has been preserved in samples with buried layers of magnesium silicide clusters grown at 650\(^\circ\text{C}\) that correspond to preservation of crystal structure of clusters inside silicon matrix. The analysis of scaling pictures of AFM images has shown the decrease of diffusion transfer of magnesium in systems with three layers at the annealing temperature \( T=650^\circ\text{C} \). The crystalline quality of cap silicon layer has increased at 750\(^\circ\text{C}\) annealing temperature but Mg\(_2\)Si clusters have not conserved in silicon matrix. It was calculated that the increase of the number of buried cluster layers up to three results in increase of \( \epsilon_{\text{eff}} \) (up to 13.0~14.5) at 0.1~6.2 eV that corresponds to increase of the contribution from transitions in three layers of magnesium silicide clusters and defect energy levels on Mg\(_2\)Si/Si interface in the electronic structure of grown layers. It was shown that an effective electron number at maximal photon energies (3.0~6.2 eV) determines the silicon contribution in the electron structure of grown cluster-based materials, but the effective number at small photon energies (0.5~2.5 eV) could be characterized by the contribution of magnesium silicide clusters and defect energy levels on Mg\(_2\)Si/Si interface. For samples with buried Mg\(_2\)Si clusters a thermoelectric power coefficient value has strongly increased up to \(- (160 \sim 360) \mu\text{V/K} \) that is \((50 \sim 180)\) times higher than that for the bare \( p \)-type silicon.

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