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Ultrathin Cr and Fe monosilicides on Si(111) substrate: formation, optical and thermoelectrical properties

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Abstract. In this study, the formation, crystal structure, optical and thermoelectric properties of ultrathin (UT) films of iron and chromium monosilicides are considered, which exhibit optical and thermoelectric properties characteristic of semimetals with a low density of states near the Fermi level and the main contribution of holes to the Seebeck coefficient in the temperature range 120–400 K and the transition to its negative values at T > 400 K. The power factor for FeSi and CrSi UT films versus temperature was calculated and ab initio calculations of the phonon structure and thermal conductivity for bulk FeSi and its nanowires were carried out, which made it possible to estimate the thermoelectric figure of merit of ultrathin FeSi films.

Keywords: silicon, Cr and Fe monosilicides, ultrathin films, crystal structure, optical functions, thermoelectric properties, power factor, ab initio calculation, thermal conductivity

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Ультратонкие моносилициды Cr и Fe на подложке Si(111): формирование, оптические и термоэлектрические свойства

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Аннотация. В данном исследовании рассмотрено формирование, кристаллическая структура, оптические и термоэлектрические свойства ультратонких пленок (УТ) моносилицидов железа и хрома, которые проявляют оптические и термоэлектрические

свойства, характерные для полуметаллов с малой плотностью состояний около уровня Ферми и основным вкладом дырок в коэффициент Зеебека в диапазоне температур 120 – 400 K и переходом к его отрицательным значениям при температурах выше 400 K. Рассчитан фактор мощности от температуры для УТ пленок FeSi и CrSi и проведены первопринципные расчеты фононной структуры и теплопроводности для объемного FeSi и его нанопроволок, что позволило сделать оценку термоэлектрической добротности УТ пленок FeSi.

Ключевые слова: кремний, моносилициды Cr и Fe, ультратонкие пленки, кристаллическая структура, оптические функции, термоэлектрические свойства, фактор мощности, первопринципные расчеты, теплопроводность

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Introduction

In recent years, there has been renewed interest in the study of monosilicides of transition metals such as Cr, Mn, Fe, and Co with the cubic structure B20 of space group $P2_13$ [1], which exhibit interesting electrical [2], thermoelectric [3] and magnetic [4] properties. Most of the experimental studies were carried out for single crystals and bulk polycrystallines. The epitaxial growth of ultrathin films on silicon may be of interest from the point of view of changes in their structure due to stresses. But the growth of films with a thickness of a few nanometers has not been previously carried out and their properties have not been studied. Also, *ab initio* calculations of thermal conductivity for FeSi nanowires have not been carried out, which does not allow one to estimate the thermoelectric figure of merit of thin-film materials.

Materials and Methods

Growth experiments were carried out in an ultrahigh vacuum setup with a base vacuum of 2×10^{-10} Torr, equipped with a slow electron diffraction analyzer, chromium (Cr) and iron (Fe) sublimation sources, a quartz thickness gauge, a three-coordinate manipulator, and a holder for four samples. The growth of films of Cr and Fe monosilicides (CrSi and FeSi) on Si(111) KEF-1000 substrates with resistivity ρ = 1000 Ohm×cm (FZ1000) was carried out by solid-phase epitaxy (T = 350 °C) after high-temperature annealing of silicon substrates at T = 1250 °C. The calculated thickness of the deposited metal layers was 3 nm for chromium and 2 nm for iron. After unloading from the growth chamber, the morphology of the grown films was studied on a Solver P47 atomic force microscope (AFM). The reflection and transmission spectra were recorded on spectrophotometers: U-3010 (Hitachi) and VERTEX v80 (BRUKER). The structure of the films was studied by high-resolution transmission electron microscopy (HRTEM) on cross sections using a JEOL-4000EX microscope (ISP SB RAS). The thermoelectrical measurements were carried out in a He2 atmosphere in a temperature range from 80 to 473 K in a Cryotel laboratory setup (MISIS).

Ab initio calculations were carried out using the VASP package [5] within the framework of the density functional theory using the generalized gradient approximation (GGR) with a cutoff energy of 300 eV and the gamma-centered k-point scheme, unless otherwise indicated. The inclusion of non-spherical corrections was also included. Convergence was checked both in terms of the cutoff energy and in terms of the number of k-points. For ε-FeSi, the relaxation of the crystal lattice was

carried out with the scheme of k-points 12×12×12. The resulting lattice parameter was 4.448 Å, which is in good agreement with the experimental data: 4.467 Å [6]. The phonon band structure of bulk ε-FeSi was calculated within the harmonic approximation using the *Phonopy* package [7]. The elements of the dynamic matrix were determined by the finite displacement method using the VASP package. The lattice thermal conductivity, group velocity, scattering rate, and phonon mean free path are calculated in bulk ε-FeSi. The Boltzmann transport equation was solved by an iterative method using the *ShengBTE* package [8]. The lattice thermal conductivity of nanowires was calculated without solving the Boltzmann equation using the mean free path over all positions of the phonon in space and the elements of the dynamic matrix calculated for the bulk ε-FeSi using the *ShengBTE* package [8].

Results and Discussion

AFM studies of the morphology of CrSi and FeSi films showed that they are continuous and smooth with an RMS roughness of 0.3 to 1.2 nm (Fig. 1 (a, *b*)). The HRTEM images of the cross sections of two samples confirmed the continuity of the ultrathin films and their small thickness (CrSi: 3.2 nm and FeSi: 2.85 nm) (Fig. 1 (*d*, *e*)), which proves good agreement with the calibration data of the metal deposition rate. Some inhomogeneity of their HRTEM images is caused by the oxidation of its upper layer after unloading from the growth chamber and storage for a month before sample preparation for HRTEM. The film/Si interface is not atomically smooth, which indicates the use of Si atoms from the substrate during film formation. The FFT images of the films (Fig. 1, *c*), showed reflections from CrSi and FeSi silicides. For individual CrSi (FeSi) nanograins, there are epitaxial relations: CrSi(210)‖Si(111) и CrSi[001]‖Si[1$\bar{1}$0] (FeSi(111)‖Si(111), FeSi[1$\bar{1}\bar{2}$]‖Si[1$\bar{1}$0] и FeSi[1$\bar{1}$0]‖Si[11$\bar{2}$]). It has been established that grains in FeSi and CrSi films are in a deformed state when coupled with the silicon lattice according to XRD data: the FeSi crystal lattice is stretched by 2.16–2.21%, and the CrSi crystal lattice is compressed by 1.78–2.69%.

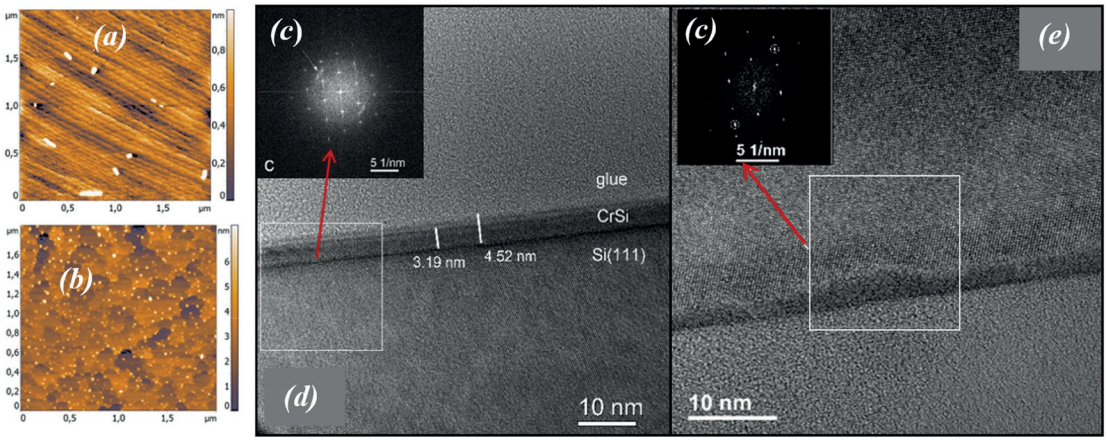

Fig. 1. AFM images of CrSi (*a*) and FeSi (*b*) film's surfaces morphology and crystal structures HRTEM images of two different cross-sectional fragments of CrSi/Si(111) (*b*) and FeSi-Si(111) (*e*) film heterosystems. The insets show the FFT patterns (*c*) from the areas marked with white squares on (*d*) and (*e*)

According to the transmission and reflection spectra for ultrathin CrSi and FeSi films (Fig. 2, *a*) in the transparency region of the silicon substrate, their refractive index and extinction spectra were calculated (Fig. 2, *b*) using the RT procedure [9]. It has been established that the spectra of the absorption coefficients of both films (Fig. 2, *c*) depend almost linearly on the photon energy, which is associated with the semimetallic or bad-metal nature of absorption with a small overlap of bands at the Fermi level and somewhat above it.

Resistivity (Fig. 3, *a*) and thermoelectric (Fig. 3, *b*, *c*) measurements for samples with CrSi and FeSi ultrathin films in the temperature range of 120–450 K showed that the Seebeck coefficient remains positive (50–200 μV/K) up to 400 K and then (at 400–470 K) changes sign to negative. Despite the four-fold excess of the resistivity for the FeSi film compared to the CrSi film in the

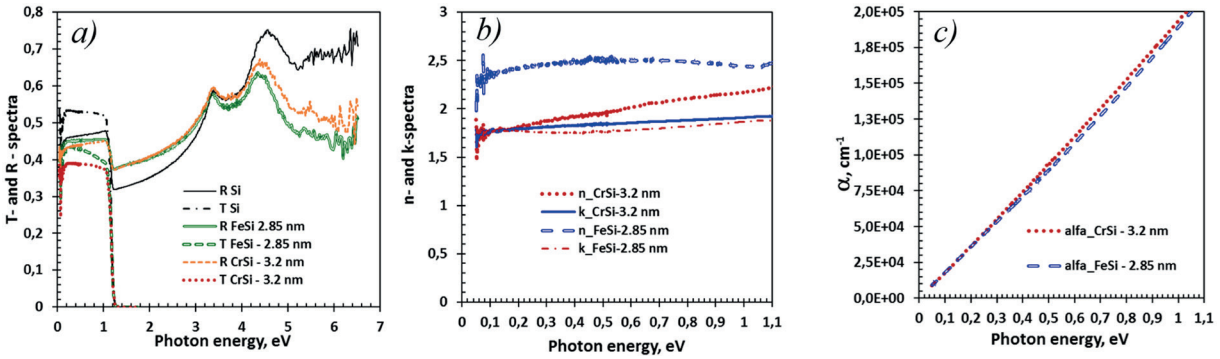

Fig. 2. Reflectance (R) and transmission (T) spectra (*a*), the refractive index and extinction coefficient spectra (*b*) of the Si substrate and samples with ultrathin films of FeSi (2.85 nm) and CrSi (3.2 nm) and transmission coefficient spectra (*c*) calculated for FeSi and CrSi films

range from 100 K to 440 K, the Seebeck coefficient for the CrSi film rapidly decreases with increasing temperature and at $T = 300$ K is compared with that for the FeSi film and then has the same temperature range from positive to negative values. At the same time, the contribution of the substrate cannot be the main one over the entire temperature range, since it has an extremely large and negative Seebeck coefficient (from −300 μV/K at $T = 470$ K to −1500 μV/K at $T = 280$ K) [10]. That is, the contribution to the Seebeck coefficient is determined by the carriers in the CrSi and FeSi films: first holes in the range from 120 K to 430 K, and then electrons from 440 K to 450 K. The temperature dependences of the power factor (PF) (Fig. 3, *c*) were calculated and it was shown that its maximum value of PF = 5 mW/(m×K^2) at a temperature of 250 K is observed for an ultrathin FeSi film with a thickness of 2.85 nm, while for a CrSi film it sharply increases to PF = 4.5 mW/(m×K^2) with decreasing temperature.

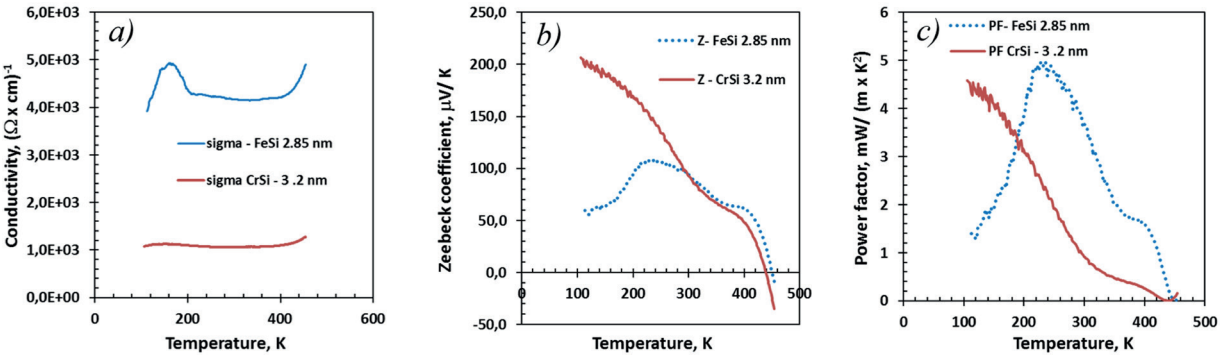

Fig. 3. Temperature dependences of electrical conductivity (*a*), Seebeck coefficient (*b*) and power factor (*c*) for samples with ultrathin films of FeSi (2.85 nm) and CrSi (3.2 nm)

The obtained values of the power factor for ultrathin films are comparable with the best values for known promising thermoelectric materials (Bi_2Te_3, $Bi_{0.5}Sb_{1.5}Te_3$, SnSe with PF = 3.0−4.5 mW/(m×K^2) [11−13]), which proves the promise of transition metal monosilicides as thermoelectrics at temperatures from 100 K to 300 K.

To estimate the lattice thermal conductivity, work was carried out on *ab initio* calculations of the phonon structure, group velocity of vibration modes, phonon scattering velocity, and phonon mean free path for cubic FeSi, both in the bulk state and in the form of nanowires. Preliminary results showed that the thermal conductivity of these objects in the range of 200−300 K varies from 10 to 15 W/m×K for bulk FeSi and from 3 to 4 W/m×K for nanowires, which gives an estimate of ZT = 0.4−0.5 at 200−250 K for nanowires, which are close to ultrathin films. The results of the calculations will be published in more detail in another article.

Conclusion

Ultrathin CrSi and FeSi films with thicknesses of 2.85−3.2 nm on silicon with (111) orientation were grown by solid-phase epitaxy at a temperature of 350 °C. The epitaxial orientations for

both films were established from the HRTEM data and their deformations were established. It was shown that the films have a semimetallic nature of absorption at photon energies up to 1.1 eV. During thermal generation of carriers in films, along with a significant Seebeck coefficient ((50−200 μV/K) at temperatures from 100 to 400 K, record values of the power factor of 4−5 mW/(m×K^2) were observed. Preliminary *ab initio* calculations of the phonon structure and thermal conductivity of bulk FeSi and its nanowires have been carried out, and a 5-fold decrease in thermal conductivity for nanowires compared to bulk material has been obtained. The thermoelectric figure of merit for FeSi nanowires (ZT = 0.4−0.5 at 200−250 K) was estimated using theoretical data on thermal conductivity, which indicates their prospects as low-temperature thermoelectric converters.

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