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CoSi ultrathin films on Si(111) substrate: comparison of the stage formation in ultra-high vacuum and during annealing in argon

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Abstract. As a result of the study, optimal conditions were identified for the formation of ultrathin films of cobalt monosilicide (CoSi) on a silicon substrate during a single annealing ($T = 500-600$ °C) of chromium layers (2–10 nm), both under ultra-high vacuum conditions and in an argon environment during isochronous annealing. The formation of the phase composition in ultrathin CoSi films is uniquely controlled in situ during growth in ultrahigh vacuum by the appearance of a bulk plasma frequency peak at 20.2–20.3 eV in the EELS spectrum, a Raman peak at 198 (204) cm^{-1} in ex situ Raman studies of the annealing in an argon environment (in vacuum) and characteristic of CoSi optical functions of refractive index and extinction and optical phonons at 223.7, 302.5 and 418.6 cm^{-1}. It has been established that cobalt films not subjected to thermal annealing in a vacuum begin to oxidize when annealed in an argon environment, which is convenient to monitor by the appearance of Raman peaks at 187 cm^{-1} and 670-677 cm^{-1}.

Keywords: cobalt layer, cobalt monosilicide, ultrathin films, isochronous annealing, ultra-high vacuum, argon environment, electronic structure, phonon structure, optical properties

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Сверхтонкие пленки CoSi на подложке Si(111): сравнение стадий формирования в сверхвысоком вакууме и при отжиге в аргоне

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Аннотация. Выявлены оптимальные условия формирования ультратонких пленок моносилицида кобальта (CoSi) на кремниевой подложке в процессе однократного отжига ($T = 500-600$ °C) слоев хрома (2–10 нм), как в условиях сверхвысокого вакуума, так и в аргоновой среде при изохронных отжигах. Формирование фазового состава в ультратонких пленках CoSi однозначно контролируется *in situ* при росте в сверхвысоком вакууме по появлению пика объемной плазменной частоты при 20,2–20,3 эВ в спектре ХПЭЭ, КРС пика при 198 (204) см$^{-1}$ при *ex situ* КРС исследованиях отжига в аргоновой среде (в вакууме) и характерных для CoSi оптических функций коэффициентов преломления и экстинкции и оптических фононов при 223,7, 302,5 и 418,6 см$^{-1}$. Установлено, что окисление пленок кобальта удобно контролировать при отжиге в среде аргона по появлению КРС пиков при 187 см$^{-1}$ и 670–677 см$^{-1}$.

Ключевые слова: слой кобальта, моносилицид кобальта, ультратонкие пленки, изохронный отжиг, сверхвысокий вакуум, среда аргона, электронная структура, фононная структура, оптические свойства

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Introduction

An urgent task is to study monosilicides of transition metals, such as Cr, Mn, Fe and Co, with a B20 cubic structure with space group P213 and breaking the symmetry of spatial inversion [1]. In addition, cobalt monosilicide (CoSi) is a topological Weyl semimetal [2] with interesting electrical and thermoelectric properties [3]. Research was mainly carried out on single crystals and bulk polycrystals of CoSi [3–6]. At the same time, the issue of the formation of thin (25–700 nm) CoSi films remains poorly studied at present [7, 8]. While ultrathin films (4–20 nm) and their formation by solid-phase epitaxy on silicon remain unstudied, both by *in situ* methods and by ex situ non-destructive phase- and structure-sensitive methods. Before proceeding to the study of the topological properties of ultrathin CoSi films, it is necessary to accurately establish the limits of temperature annealing of ultrathin cobalt films on silicon for the formation of CoSi, their phase homogeneity and temperature stability, which is the focus of this work. Also, CoSi, as shown in works [2, 3], despite their semi-metallic properties, are a promising material for thermoelectric converters in bulk form and in the form of thin epitaxial films on silicon.

Materials and Methods

Experiments on the deposition of ultra-thin Co layers were carried out on Varian ultra-high vacuum (UHV) units and UHV *A*-chambers with a base vacuum of 2×10^{-10} Torr, equipped, respectively, with an Auger electron spectroscopy (AES) and electron energy loss spectroscopy (EELS) analyzer and a diffractometer of low energy electrons (LEED), as well as sources of cobalt (Co) and silicon (Si). Before the growth of Co films, an atomically-clean surface of silicon substrate (Si(111)7×7) was formed. Silicon cleaning consisted of two stages: long-term (5–6 hours) degassing at $T = 650$°C and high-temperature short annealing at $T = 1150$ °C with a total duration of 5 minutes [9], followed by monitoring of the AES and EELS spectra or LEED patterns. In the first experiments, Co layers 2–10 nm thick were deposited at room temperature on the Si(111)7×7 surface. Initially, for a number of samples, solid-phase annealing was carried out in a UHV *A*-chamber at temperatures from 400 °C to 500 °C according to the data of CoSi formation temperature [7, 8]. In a Varian UHV chamber, in order to determine the CoSi formation temperature, isochronous annealing of a Co film with a thickness of 7.7 nm was carried out at temperatures from 275 °C to 700 °C with a step of 25 °C and step-by-step recording of the AES and EELS spectra. Individual Co films were unloaded without annealing, and then annealed in a special attachment (Linkam THMS600) in the temperature range (30–550 °C, step 25 °C) with argon purging and simultaneous recording of Raman spectra (RS) on the NTEGRA SPECTRA II installation to control the onset of formation CoSi and its saturation. This setup was also used to record Raman spectra for a number of CoSi films formed by solid-phase annealing in UHV chambers. To control the optical properties and phonon structure of CoSi films, reflection and transmission spectra were recorded on spectrophotometers: U-3010 (Hitachi) and VERTEX v80 (BRUKER).

Results and Discussion

In order to determine the optimal formation temperature of a CoSi film, AES and EELS spectra were recorded and analyzed for a 7.7 nm thick Co layer at different annealing temperatures (Fig. 1, *a*, *b*). It has been established that the formation of CoSi begins at a temperature of 325 °C, which is confirmed by changes in the intensities of the AES spectra for Co and Si (Fig. 1, *a*) and shifts of the peaks from the initial positions (not shown), which corresponds to the entry of Co and Si into a chemical bond and a decrease in Co concentration and an increase in Si concentration (Fig. 1, *a*). The composition of the silicide, close to stoichiometric CoSi, is formed at temperatures of 400–600 °C (Fig. 1, *a*). More precisely, the phase composition is confirmed by the EELS spectra (Fig. 1, *b*), when surface (13.3 eV) and bulk (20.2–20.5 eV) plasmons corresponding to CoSi [10] are formed in the temperature range 400–600 °C. The transition from CoSi to $CoSi_2$ is observed at temperatures above 675 °C, which corresponds to a shift of the bulk plasmon to the position of 19.3 eV (Fig. 1, *b*), corresponding to $CoSi_2$ [10, 11]. The maximum bulk plasmon intensity of 20.2–20.2 eV is observed in the temperature range of 500–600 °C, which corresponds to the formation of the maximum amount of the CoSi phase and its best crystalline state, and also does not fully correlate in terms of the annealing temperature of Co layers with previously obtained data [7, 8].

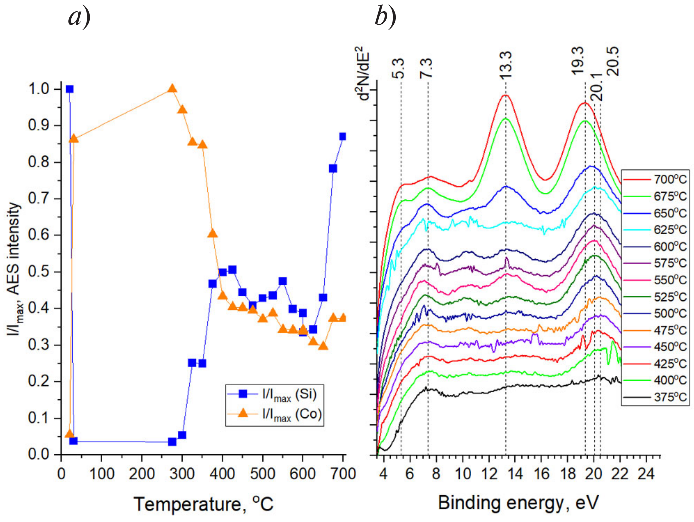

Fig. 1. Dependences of Co and Si concentrations by AES intensities data on annealing temperature (*a*); changes in the EELS spectra with increasing annealing temperature. Al data are presented for the Co film d_{Co} = 7.7 nm grown by SPE method at T = 275–700 °C (*b*)

Registration of Raman spectra during annealing of a Co film (4.8 nm) on Si substrate in an argon environment, unloaded from an UHV chamber without a protective layer (Fig. 2, *a*), confirmed the lower limit of the CoSi formation temperature (325 °C), when a Raman peak appears at 198 cm^{-1} that close to 204 cm^{-1} for CoSi films [12]. The maximum intensity of the Raman peak at 198 cm^{-1} is observed with increasing annealing temperature to 475–500 °C, which corresponds to the maximum amount of the formed CoSi phase (Fig. 2, *a*) and correlates with in situ control data: AES and EELS (Fig. 1, *a*, *b*, *c*, *d*). Simultaneously with the growth of the CoSi phase, the formation of peaks at 187 cm^{-1} and 677 cm^{-1} is observed, starting from a temperature of 375 °C, which correspond to the formation of Co oxide, which correlates with the data of [13], in which in the Raman spectra

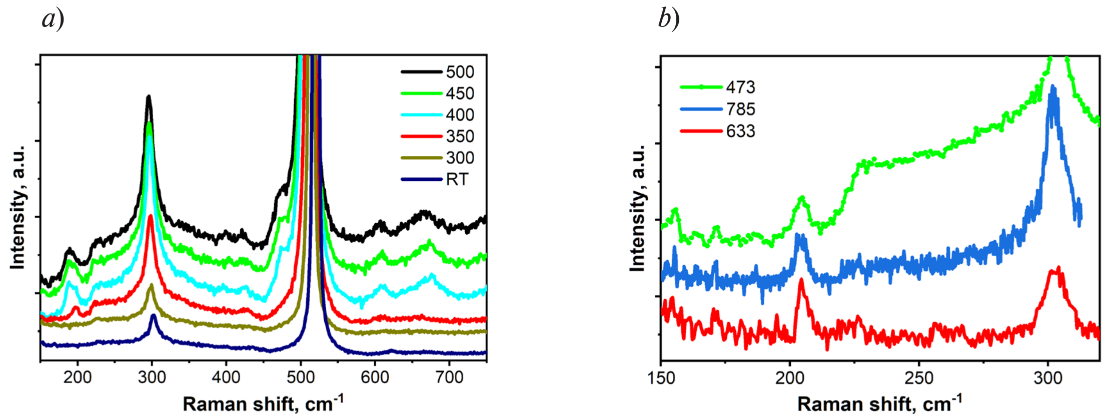

Fig. 2. Raman spectra at a laser wavelength of 785 nm at different annealing temperatures (300–500 °C) of the Co film (d_{Co} = 4.8 nm) (*a*). Raman spectra at laser wavelengths at 473, 633 and 785 nm for Co layer (4 nm) grown by SPE at 500 °C in UHV chamber (*b*)

during oxidation in argon or oxygen environment, peaks appeared at 195 cm^{-1} and 670–690 cm^{-1} during the annealing of the Co film. The intensity of the peaks at 187 cm^{-1} and 677 cm^{-1} (Fig. 2, *a*) increased with increasing annealing temperature in argon, which corresponds to an increase in the thickness of the cobalt oxide layer. Presumably, Co oxide is formed due to the decomposition of $Co(OH)_2$ formed on top of the Co layer after the sample with the Co film was unloaded into air without a protective layer, which correlates with the data of [14], which considered stepwise annealing processes of thick Co films in air. For a Co layer 4 nm thick, after annealing in vacuum at 500 °C, a peak at 204.1 cm^{-1} and additional weak peaks at 223.8 cm^{-1} and 242.1 cm^{-1} appear in the Raman spectra (Fig. 2, *b*), which corresponds to the data of work [12].

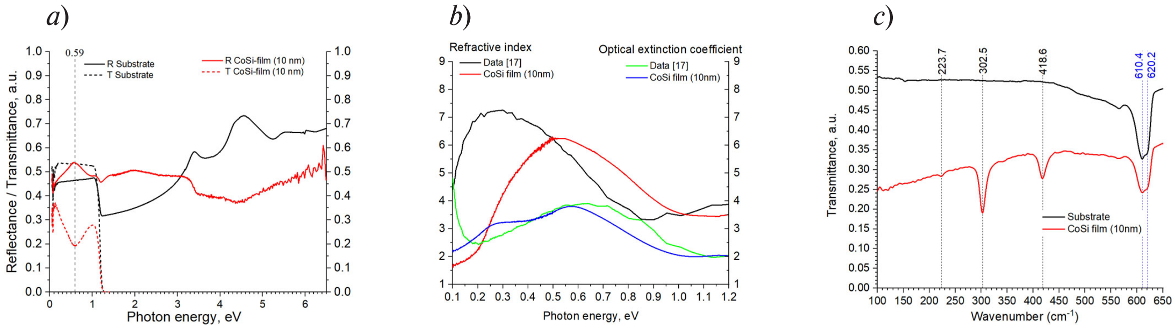

Fig. 3. Optical reflectance (*R*) and transmittance (*T*) spectra in UV-VIS-MIR range for grown CoSi films (10 nm of Co) and Si substrate (*a*), refractive index (*n*) and optical extinction coefficient (*k*) calculated for CoSi film and for CoSi bulk [17] (*b*) and *T*-spectra in the far infrared range (FIR) for CoSi film with Co thickness of 10 nm and Si substrate (*c*)

Registration of reflection spectra (*R*) and transmission spectra (*T*) (Fig. 3, *a*) showed that the CoSi film has a low reflectance in the mid- and near-IR ranges (0.2–1.1 eV), which is typical for materials usually, semiconductors [15] and semimetals such as CoSi [1, 2]. As the photon energy decreases (0.05–0.1 eV), a noticeable decrease in transmission is observed (Fig. 3, *a*), which is associated with an increase in the absorption coefficient for free carriers in "pockets" above and below the Fermi level [1–3]. Calculations of the refraction and extinction coefficient spectra within the framework of the two-layer model [16] showed (Fig. 3, *b*) not bad agreement with the data for bulk CoSi samples due, the optical properties of which were studied by spectral ellipsometry [17], which also proves the single-phase nature of the ultrathin CoSi films. FIR spectral data (Fig. 3,*c*) also confirmed the formation of CoSi with phonon peaks at 223.7, 302.5 cm^{-1} and 418.6 cm^{-1}, the amplitudes of which increase with the thickness of CoSi (not shown) and which belong to CoSi according to the literature [18].

Conclusion

Based on AES, EELS and Raman data, the temperature range (400–600 °C) for the formation of ultrathin CoSi films on a Si(111) substrate upon annealing of Co layers with a thickness of 2–10 nm was determined. It has been established that the maximum intensity of bulk plasmon peaks in the EELS spectra is observed at the temperatures of 500–600 °C. It was shown that UHV annealing and annealing in an argon environment lead to similar results, which is confirmed by both AES-EELS spectra, Raman spectroscopy and optical spectroscopy data. Raman data revealed the influence of a $Co(OH)_2$ layer adsorbed on Co in air on the formation of Co oxide. The dependences of the refractive index and extinction coefficient on the wavelength calculated from the optical spectra for ultrathin CoSi films are in not bad agreement with the data for bulk CoSi, which confirms their semi-metallic nature of the band energy structure. FIR spectroscopy data confirm the formation of ultrathin CoSi films, both after annealing Co layers in an ultra-high vacuum, and after annealing Co films in an argon environment after unloading from the UHV chamber.

REFERENCES

1. **Dutta P.**, **Pandey S.K.**, Investigating the electronic structure of MSi (M = Cr, Mn, Fe &Co) and calculating U_{eff} & J by using cDFT, Computational Condensed Matter. 16 (2018) e0035 (1–7).

2. **Pshenay-Severin D.A., Ivanov Y.V., Burkov A.A., Burkov A.T.**, Band structure and unconventional electronic topology of CoSi, Journal of Physics: Condensed Matter. 30 (2018) 135501.

3. **Pshenay-Severin D.A., Ivanov Yu. V., Burkov A.T., Novikov S.V., Zaitsev V.K.**, **Reith H.**, Electronic Structure and Thermoelectric Properties of Transition Metal Monosilicides, Journal of Electronic Materials. 47 (2018) 3277–3281.

4. **Ou-Yang T.Y., Shu G.J., Fuh H.R.**, Thermoelectric performance and electronic properties of transition metal monosilicides, EPL. 120 (2017) 17002.

5. **Schnatmann L., Lammel M., Damm C., Levin A.A., Pérez N., Novikov S., Burkov A., Reith H., Nielsch K., Schierning G.**, Crystal Structure Analysis and Magneto-Transport Investigation of $Co_{1-x}Fe_xSi$ (with $x = 0\%$ to $x = 20\%$), Adv. Electron. Mater. 8 (2022) 2101081.

6. **Salamatin D.A., Bokov A.V., Kozin M.G., Romashkina I.L., Salamatin A.V., Mikhin M.V., Petrova A.E., Sidorov V.A., Nikolaev A.V., Fisk Z., Tsvyashchenko A.V.**, Anomalous Positron Lifetime in Single Crystal of Weyl Semimetal CoSi, Crystals. (13) (2023) 509.

7. **Normuradov M.T., Bekpulatov I.R., Imanova G.T., Igamov B.D.**, Structures for constructing devices from formed Mn_4Si_7 and CoSi films, Advanced Physical Research. 4 (2022) 142–154.

8. **Li Z., Yuan Y., Hübner R., Rebohle L., Zhou Y., Helm M., Nielsch K., Prucnal S., Zhou S.**, B20 Weyl Semimetal CoSi Film Fabricated by Flash-Lamp Annealing, ACS Applied Materials & Interfaces. 15 (2023) 30517–30523.

9. **Galkin N.G., Migas D.B., Medvedeva N.V., Filonov A.B., Dotsenko S.A., Maslov A.M., Chernev I.M, Subbotin E.Yu, Goroshko D.L., Samardak A.Yu., Gutakovskii A.K., Tkachenko I.A., Gerasimenko A.V.**, New monoclinic ground state of FeSi, Comp. Mater. Science. 233 (2024) 112762.

10. **Plusnin N.I., Milenin A.P., Prihod'ko D.P.**, Formation of the CoSi(111)7×7 interface: AES- and EELS-study. Applied Surface Science. (166) (2000) 125–129.

11. **De Crescenzi M., Derrien J., Chainet E., Orumchian K.**, Core-level electron-energy-loss spectroscopy as a local probe for the electronic structure of the Co/Si(111) interface, Physical Review B. 39 (8) (1989) 5520.

12. **Racu A.-M., Menzel D., Schoenes J., Doll K.**, Crystallographic disorder and electron-phonon coupling in $Fe_{1-x}Co_xSi$ single crystals: Raman spectroscopy study, Physical Review B. 76 (11) (2007) 115103.

13. **Liu F.M., Ye J.H., Ren B., Yang Z.L., Liao Y.Y., See A., Chan L., Tian Z.Q.**, Raman spectroscopic studies of the formation processes of cobalt silicide thin films, Thin Solid Films. 471(1–2) (2005) 257–263.

14. **Tompkins H.G., Augis J.A.**, The oxidation of cobalt in air from room temperature to 467 °C, Oxidation of Metals. 16 (5–6) (1981) 355–369.

15. **Seeger K.**, Semiconductor Physics, Springer Science & Business Media. 2013.

16. **Galkin N.G., Maslov A.M., Konchenko A.V.**, Optical and photospectral properties of $CrSi_2$ A-type epitaxial films on Si(111), Thin Solid Films. 311(1–2) (1997) 230–238.

17. **Van der Marel D., Damascelli A., Schulte K., Menovsky A.A.,** Spin, charge, and bonding in transition metal mono-silicides, Physica B: Condensed Matter. 244 (1) (1998) 138–147.

18. **Acun A.D., Soyalp F.,** Elastic and phonon properties of FeSi and CoSi in the B2 structure, Philosophical Magazine. 92 (5) (2012) 635–646.

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