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Ellipsometric evidence of $CoSi_2$ formation in Co/Si multilayer induced by thermal annealing

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The work aim is to demonstrate the potential of the spectroscopic ellipsometry (SE) approach to study the solid state reactions, both spontaneous and/or induced by thermal annealing, in (3.0 nm Co / 10.6 nm $Si)_{20}$ multilayered film (MLF). The regions with a stoichiometry close to Co_2Si are supposed to be formed spontaneously in the as-deposited Co/Si MLF. Sequential anneals of Co/Si MLF at 400, 600, and 700°C do not produce any visible changes in their amorphous-like large-angle X-ray diffraction (HAXRD) spectra, while the SE indicates the formation of regions with a stoichiometry close to CoSi. Independently on the HAXRD results, the conclusion on the formation of $CoSi_2$ phase induced by annealing of Co/Si MLF at 800°C can be confidently done on the basis of only optical study.

Целью работы является демонстрация возможностей спектроскопической эллипсометрии (SE) при исследовании твердофазных реакций (как самопроизвольных, так и индуцированных) в многослойной пленке (MLF) (3,0 нм Co / 10,6 нм Si)20. Предполагается, что в свежеосажденной области Co/Si MLF самопроизвольно образуются области со стехиометрией, близкой к Co_2Si. Последовательный отжиг Co/Si MLF при 400, 600 и 700°C не вызывает видимых изменений в спектрах широкоугловой дифракции рентгеновских лучей (HAXRD), в то время как SE выявляет образование областей со стехиометрией, близкой к CoSi. Независимо от результатов HAXRD, на основании только оптических исследований можно сделать надежный вывод об образовании фазы $CoSi_2$ под влиянием отжига Co/Si MLF при 800°C.

Metal silicides have drawn a great attention in connection with VLSI-devices for interconnectors, gate, and source contacts due to low resistivity, good thermal stability and small mismatch with Si substrate. Among the metal silicides, cobalt disilicide is distinguished by the lowest resistivity. $CoSi_2$ films are commonly prepared by evaporation or sputtering of the single Co layer onto Si substrate, or formation of Co/Si multilayered film (MLF) of appropriate stoichiometry followed by a subsequent annealing. The reaction proceeds usually through a number of intermediate phases until the thermally stable end product is reached. It was found that the sequence of phase formation as well as the temperatures of their appearance depend on the layer and sublayer thicknesses. Thus, for example, when annealing a thick (about 100 nm or thicker) Co film deposited onto Si substrate Co_2Si phase is formed first [1], while for

the (polycrystalline Co/amorphous Si) MLF with overall stoichiometry of 1:2 and bilayer period of about 80 nm, CoSi was found to be formed as the first silicide phase, and next Co_2Si, CoSi, and $CoSi_2$ phases are formed sequentially as the annealing temperature increases [2]. On the other hand, for very thin (up to 4 monolayers) Co layers on Si, it is just $CoSi_2$ phase that was found to be formed first at $T \geq 350$°C [3].

The initial silicide growth stage and reaction mechanism are usually studied using surface sensitive methods such as X-ray diffraction, XPS, RBS, SIMS, AES, and LEED. It is well known that both optical and magneto-optical (MO) properties of metals depend strongly on their electron energy structures which are correlated with the atomic and magnetic ordering. The spontaneous or thermally induced interdiffusion between Co and Si atoms in the Co/Si MLF should change the chemical and atomic ordering in the reactive zone and also decrease the thickness of Co sublayers (and hence the MO response from the layered system). So, it seems attractive to employ noncontact nondestructive spectroscopic ellipsometry (SE) and MO spectroscopy for *in situ* studying the solid state reactions in the layered structures. The ellipsometry was already employed for the investigation of cobalt silicides formation induced by annealing of Co layers deposited on Si wafer [4–6]. However, the authors have performed only ellipsometric measurements at fixed wavelength [5], or restricted the SE investigations only to cosΔ spectra measurements [4] (where Δ is the ellipsometric angle), or obtained the variation of volume fractions of two possible Co-silicide phases with depth in the framework of Bruggeman effective medium theory without the multilayer model parametrization [6].

Obviously, the real structures and magnetic properties of the as-deposited and/or reacted layered (or multilayered) system may be verified by a comparison between the experimental and computer-simulated optical and MO data, based on an appropriate model of the layered structure and the properties of the constituent sublayers. The optical properties of crystalline cobalt monosilicide [7] and disilicide [8–12] were studied experimentally several times and explained using the results of first-principles calculations [12]. This fact creates the favorable conditions for the comparison of optical properties of the reacted Co/Si MLF with those of crystalline cobalt silicides. Thus, the aim of this work is to demonstrate the potential of the optical approach (SE and MO spectroscopy) for studying of the spontaneous solid state reactions and those induced by thermal annealing in Co/Si MLF.

$(3.0$ nm Co$/10.6$ nm Si$)_{20}$ MLF with overall stoichiometry of $CoSi_2$ and Co topmost layer were prepared by DC-sputtering onto single-crystalline Si substrates kept at room temperature (RT). The structural characterization of the Co/Si MLF in the as-deposited state and after each step of heat treatment was performed by HAXRD with Co K_α radiation using the Debye-Sherrer photographic camera. The details of the optical and MO measurements can be found elsewhere [13]. After the structural and physical properties of the as-deposited Co/Si MLF had been investigated, the MLF were annealed in sequence at 400, 600, 700 and 800°C and their structural and physical properties were studied again after each annealing step. The simulation of the optical and MO properties of the Co/Si MLF have been performed by exact solving the multireflection problem by using a scattering matrix approach [14]. The simulation needs the knowledge of the optical and MO properties of constituent sublayers of the Co/Si MLF (as input parameters for simulation). For this purpose, pure Co and Si films of 100 and 650 nm thickness, respectively, were deposited at the same deposition conditions and their dielectric functions (DF) were determined. In addition to Co and Si films, an amorphous $Co_{0.33}Si_{0.67}$ alloy film and a polycrystalline bulk $CoSi_2$ alloy sample were prepared and their optical properties were investigated. An amorphous $Co_{0.33}Si_{0.67}$ alloy film was prepared using flash evaporation of the $CoSi_2$ alloy powder onto glass substrate cooled with liquid nitrogen.

The HAXRD spectrum of the as-deposited Co/Si MLF (not shown) looks amorphous-like. The experimental OC and ε_1 spectra for the Co/Si MLF in the as-deposited state and after various heat treatments are shown in Fig. 1. It is clearly seen that all these spectra might be subdivided into three different groups as to behavior: the first group includes the σ and ε_1 spectra for the as-deposited state, the second group is formed by the spectra obtained after annealing at 400, 600 and 700°C, and the last one answers to the state formed due to annealing of the Co/Si MLF at 800°C. The OC

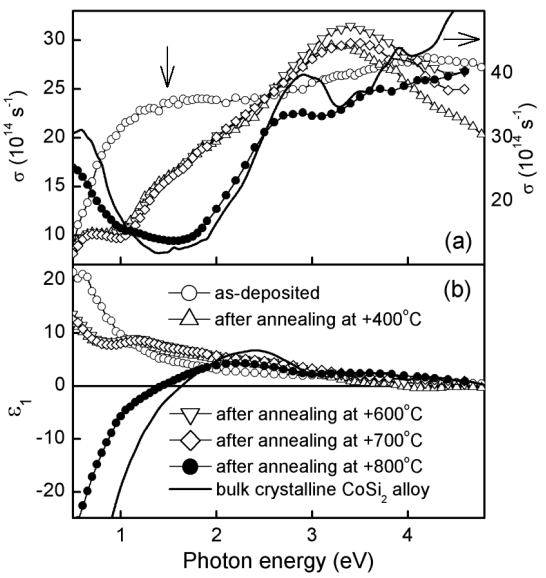

Fig. 1. Experimental optical conductivity (a) and ε_1 (b) spectra for the (3.0 nm Co/10.6 nm Si)$_{20}$ MLF in the as-deposited state and after various heat treatments. The corresponding spectra for bulk crystalline $CoSi_2$ alloy are shown by solid lines for the comparison.

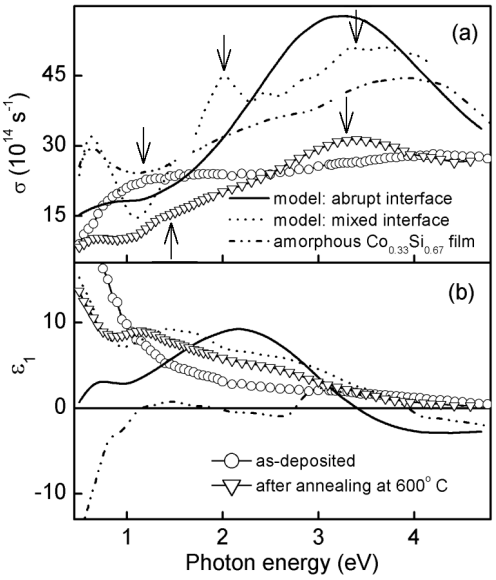

Fig. 2. Experimental (symbols) and simulated for different models (see text) (lines) optical conductivity (a) and ε_1 (b) spectra for (3.0 nm Co/10.6 nm Si)$_{20}$ MLF. The experimental σ and ε_1 spectra for amorphous $Co_{0.33}Si_{0.67}$ alloy films are shown by dash-dot-dot lines.

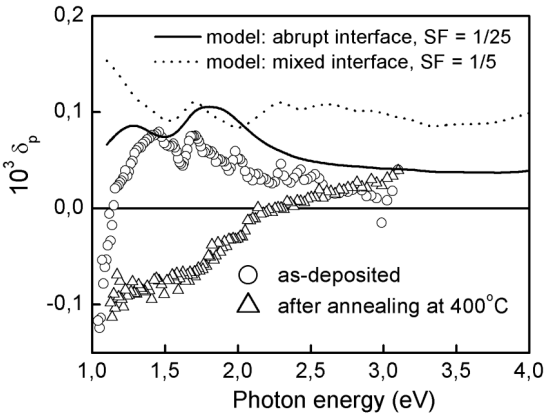

Fig. 3. Experimental (symbols) and simulated (lines) for different models (see text) EKE spectra for (3.0 nm Co/10.6 nm Si)$_{20}$ MLF taken at RT and the angle of incidence of 66°.

spectrum for the as-deposited Co/Si MLF is structureless in the 1.5 to 4 eV energy range with a sharply decreasing σ value below 1.5 eV. The ε_1 (being always positive) shows a steady increase with the decreasing photon energy. The formation of the homogeneous amorphous structure in the as-deposited Co/Si MLF should be excluded from the consideration, because optical properties of homogeneous amorphous $CoSi_2$ film (especially the ε_1 spectra) differ markedly from those of MLF's (see Fig. 2). The simulated OC spectrum for the Co/Si MLF obtained for the model with a sharp interface between pure Co and Si sublayers of nominal thicknesses (see Fig. 2) exhibits a prominent absorption peak near 3.1 to 3.3 eV (formed from the Si-subalyers) and a weak singularity at 0.9 eV which is originated from the main interband absorption peak of Co. The experimental OC spectrum of the as-deposited Co/Si MLF does not show any visible evidences of the 3.1 eV absorption peak related to amorphous Si. This fact, as well as the drastic shape disagreement between the simulated and experimental ε_1 spectra enable us to conclude that the aforementioned model of the Co/Si MLF does not describe adequately the actual MLF's structure. The same categorical conclusion on lack of correspondence of such a Co/Si MLF model to the reality arises also from the comparison of the experimental and simulated EKE spectra. The experimental MO response from the as-deposited Co/Si MLF is extremely weak, and the simulated EKE spectrum should be plotted with a scaling factor of 1/30 in order to make their magnitudes comparable (see Fig. 3).

Both these results can be understood if the noticeable reduction of pure Si and Co contents in such a films due to intermixing

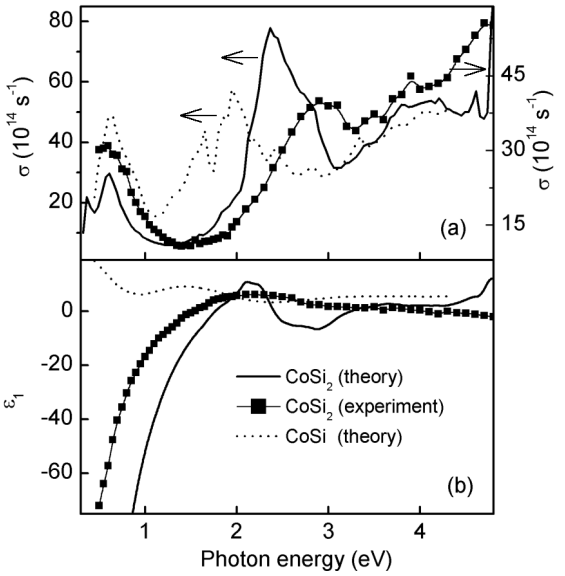

Fig. 4. Calculated (lines) and experimental (symbol) σ (a) and ε_1 (b) spectra for CoSi [15] and $CoSi_2$ [12] silicides.

or cobalt silicide formation will be supposed. This is consistent with results of Fallon et al. who observed the superparamagnetic behavior in co-deposited $Co_{1-x}Si_x$ alloy films for $x > 0.40$ [15]. The agreement between the simulated and the experimental OC spectra for the as-deposited Co/Si MLF is not significantly improved if the complete consumption of Co sublayers and partial consumption of the Si sublayers for the cobalt silicide formation of CoSi stoichiometry will be supposed (see Fig. 2). In such a model (so-called "mixed interface model"), the (3.0 nm Co/10.6 nm Si)$_{20}$ MLF's formula was replaced by the (8.46 nm CoSi/5.14 nm Si)$_{20}$ one. As input parameters for CoSi sublayers, the results of the first-principles calculations of the optical properties of the CoSi compound were used (see Fig. 4). It is known that CoSi is not ferromagnetically ordered at RT [16]. Therefore, to simulate the EKE spectrum of the as-deposited Co/Si MLF in the framework of essentially the same model with mixed interface of CoSi stoichiometry, we supposed that only 2 monolayers of pure Co were remained unreacted. For this case, the Co/Si MLF structure might be presented as: (3.93 nm CoSi/0.3 nm Co/3.93 nm CoSi/5.54 nm Si)$_{20}$. However, even for this model, the scaling factor of about 1/10 should be used in order to equalize the magnitudes of the experimental and simulated EKE spectra (see Fig. 3).

Taking into account the trend in main absorption peak location in the OC spectra of Co-silicides (see Fig. 4) and Ni-silicides [17] with increase in 3*d*-TM content, the singularity at 1.5 eV in the OC spectrum of as-deposited Co/Si MLF might be related to the formation of regions with a stoichiometry close to Co_2Si. Annealings of the as-deposited Co/Si MLF at 400, 600, and 700°C do not produce any visible changes in their amorphous-like HAXRD spectra. However, the optical properties of the Co/Si MLF are changed very significantly while being essentially identical to each other (see Fig. 1). The comparison of the experimental σ and ε_1 spectra for the Co/Si MLF annealed at 600°C with the simulated ones made for mixed interface model and MLF formula of (8.46 nm CoSi/5.14 nm Si)$_{20}$ shows the considerable resemblance thereof. This enables us to conclude that annealing at 400, 600, and 700°C results in Co_2Si conversion into CoSi. This is also consistent with the statement of Pretorius and Mayer that the CoSi phase is followed by the Co_2Si one formed first [18]. It should be reminded here that in simulation, we used the results of first-principles calculations for CoSi, which were not broadened. That is why the interband absorption peaks in the simulated σ spectrum look sharper than those of experimental OC spectrum.

The EKE spectrum for the annealed Co/Si MLF is noticeably different from that of the as-deposited one (see Fig. 3). However, the magnitude of the MO response is also extremely weak. An annealing of the Co/Si MLF at 800°C causes appreciable changes in its optical properties: the interband absorption peaks at 0.7 and 1.5 to 2 eV become disappeared, and instead of a broad peak at 3.2 eV, two peaks at 2.75 and 3.6 eV are occurred in the OC spectrum of this MLF (see Fig. 1). The comparison of the experimental σ spectrum of such an annealed Co/Si MLF with that of crystalline bulk $CoSi_2$ (see Figs. 1 and 4) as well as with the results of the first-principles calculations for $CoSi_2$ compound (see Fig. 4) indicates their perfect agreement. Therefore, the conclusion on the formation of crystalline $CoSi_2$ phase in Co/Si MLF can be confidently made on the basis of these optical data. The HAXRD spectrum of the Co/Si MLF annealed at 800°C is also changed drastically showing the formation of crystalline $CoSi_2$ phase.

Thus, the consideration of the optical data enables us to conclude that as-deposited Co/Si MLF is not homogeneously amorphous, and that the Co sublayers are consumed for the formation of the regions with stoichiometry close to, probably, Co_2Si. HAXRD patterns do not show any visible changes in the Co/Si MLF's structure caused by its annealing at 400, 600 and 700°C, while according to the results of optical study, the structure of such annealed MLF differs from that of the as-deposited one and might be represented by the formula (8.46 nm CoSi/5.14 nm Si). Independently on the HAXRD results, the conclusion on the formation of $CoSi_2$ phase induced by annealing of Co/Si MLF at 800°C can be confidently done basing on the optical study only.

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Еліпсометричне посвідчення утворення Co_2Si у багатошарових плівках Co/Si під впливом термічного відпалу

Ю.В.Кудрявцев, Ю.П.Лі, Ю.Х.Гюн, Е.П.Павлова, Ю.Н.Макогон

Метою роботи є демонстрація можливостей спектроскопічної еліпсометрії (SE) при дослідженні твердофазних реакцій (як спонтанних, так і індукованих) у багатошаровій плівці (MLF) (3,0 нм Co/10,6 нм $Si)_{20}$. Припускається, що у свіжоосадженій області Co/Si MLF спонтанно утворюються області зі стехіометрією, близькою до Co_2Si. Послідовний відпал Co/Si MLF при 400, 600 і 700°C не викликає видимих змін у спектрах ширококутової дифракції рентгенівських променів (HAXRD), у той час як SE виявляє утворення областей зі стехіометрією, близькою до CoSi. Незалежно від результатів HAXRD, на підставі тільки оптичних досліджень можна зробити надійний висновок про утворення фази $CoSi_2$ під впливом відпалу Co/Si MLF при 800°C.