In situ differential reflectance spectroscopy study of solid phase epitaxy in Si(111)-Fe and Si(111)-Cr systems*

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The results of investigations devoted to a search of conditions of the simultaneous metal and semiconductor silicides formation being important problem for microelectronics are presented in the paper. The Si(111)-Fe and Si(111)-Cr systems having been chosen due to low lattice misfit of silicides observed in they were studied by the methods of Differential Reflection Spectroscopy (DRS) and Atomic Force Microscopy (AFM). The new method (Restored Standard method) having been invented for DRS studying of solid phase epitaxy (SPE) in these systems is first noted. The detailed description of processes occurred in the investigated systems and optimal conditions for the simultaneous metal and semiconductor silicides formation are presented in paper. [DOI: 10.1380/ejssnt.2006.319]

Keywords: Film growth; Iron silicide; Chromium silicide; Differential Reflectance Spectroscopy; Atomic Force Microscopy; Si(111)

I. INTRODUCTION

Silicides are promising materials for microelectronics, for example the semiconductor silicides can be used as materials of transistors and metal silicides as stable contacts to these transistors. During deposition of some metals on silicon substrates formation of both metal and semiconductor silicides takes place [1] so the transistor and contact platform can be grown during the same technological operation. The search of the conditions for simultaneous formation of metal and semiconductor silicides is one of the most important problems. Our work is devoted to solve this problem for two systems, namely Si(111)-Fe and Si(111)-Cr systems. The reason of this choice is low lattice misfit of silicides observed in these systems.

The Si(111)-Fe system is abundant of different phases. Four silicides, namely α-FeSi2, γ-FeSi2, FeSi (CsCl type) and β-FeSi2, are observed in it. The last is a direct semiconductor and its band gap (Eg = 0.87 eV) [1] is close to the optical fiber transmittance window. Therefore, this silicide is a good material for optoelectronics. Other iron silicides are metals and can be used as contact platform.

In the previous work [2] we studied iron silicide formation during reactive deposition epitaxy (RDE) at 475°C and found that simultaneous formation of FeSi and β-FeSi2 crystallities occurs at low iron coverage (below 2.0 monolayers (ML)). The next step should be studying of iron silicide formation during SPE of low coverage iron at different temperatures, in order to find optimal conditions. The results of this investigation are the 1st part of our work.

Another part is devoted to study of chromium silicides formation in the Si(111)-Cr system during SPE at different temperatures. The number of silicides in it is lower than in mentioned above system. Only two silicides, namely CrSi2 and CrSi, can be grown in it. The first is a direct semiconductor and its band gap is 0.67 eV [1]. The last is metal, and so it is the only candidate for semiconductor - metal pair. In order to know whether simultaneous formation of these silicides occurs RDE of chromium has been studied at CrSi2 formation temperature (650°C) [3]. You may have guessed form article title that the investigation being the 1st step of complex study of simultaneous chromium silicides formation has given positive results, otherwise the title must have been different.

In this work we used DRS and AFM for study of SPE. The new method, named the restored standard method, for DRS studying of SPE has been invented. It is presented in the paper first and enables to calculate variation of response function (VRF) of film at different temperatures during SPE. VRF is proportional to imaginary part of dielectric function of film and so it can be used to estimate optical properties of SPE films.

II. EXPERIMENTAL

The experiments were carried out in the ultra high vacuum (UHV) chamber Varian presented in Fig. 1 with base vacuum of the order of 2 × 10−10 Torr, equipped with an optical spectrometer (7) and halogen lamp (6) for DRS, an Auger Electron Spectrometer (Physical Electronics) (5), iron and chromium evaporation units (3) and a sample holder (1) for three silicon wafers (Si(111), p-type, 1.0 Ωcm). The samples were heated at 600°C by DC for 3 hours and finally cleaned by flashing at 1250°C for a few seconds. Cleanliness of the silicon surface was proved by Auger Electron Spectroscopy. Iron and chromium were deposited from a tungsten wire basket and a tantalum foil tube, accordingly. During the deposition the silicon...
substrate was kept at room temperature (RT). For iron deposition the rate was 0.016 nm/min, the final amount of the deposit was 0.47 nm; for that chromium one these values were 0.0224 nm/min and 0.26 nm, respectively. The deposition rate has measured by a quartz microbalance sensor (4). Further isochronous annealing of the films was done in 15 minutes at temperature range from 300 to 650°C, the step of its variation was 50°C.

Differential reflectance spectra were recorded periodically (every 12 seconds) during both metal deposition and isochronous annealing. The spectral range investigated extended from the infrared (1.1 eV) up to the visible light (2.8 eV). Morphology of the films was finally studied ex-situ by AFM.

The method of DRS has been described in detail in [4]. The method is applicable to very thin films ($d/\lambda \leq 0.05$). The basis of DRS is obtaining of the differential reflectance coefficient (DRC)

$$\frac{\Delta R}{R_{exp}} = \frac{R_a - R_s}{R_s},$$

where $R_a$ and $R_s$ are reflectance coefficients being obtained for investigated sample (with adsorbate) and standard (reference sample), respectively. Usually the initial state of sample (before or after cleaning) is used as standard. Dependence of DRC versus photon energy contains information on energy and probabilities of possible optical transitions. Two scientists having first derived the relation between the DRC and the dielectric function of a uniform film (see below, Eq. (4)) were D. E. Aspnes and J. D. E. McIntyre [5]. This expression is useful for presentation of principles of the dynamic standard method being described below. Since a percentage of samples having uniform film among investigated samples is too low, Eq. (4) is rarely used. Usually the film being studied is not uniform or is too thin (sub-monolayer films), and so for calculation is correct to use the formula [6]

$$\frac{\Delta R}{R_s} = 4\left(\frac{\omega}{c}\right) \cos \theta \cdot \text{Im}\left(\epsilon_{yy}(\omega, T)\right) \cdot \epsilon_{yy}(\omega, T) - 1,$$

where

$$\Delta \epsilon_{yy} = \int_{-\infty}^{+\infty} dz \left[\epsilon_{yy}(\omega, T) - \langle \epsilon_{yy}(\omega, T) \rangle\right]$$

is the difference of the response function for the investigated sample and standard, respectively, (its variation is called VRF) $\epsilon_{yy}(\omega, T)$ is the dielectric functions of the bulk silicon, the standard (bare substrate) and the sample with adsorbed impurities, $\theta$ - incidence angle, $c$ - light velocity, $\omega$ - light frequency and $T$ - temperature of both investigated sample and standard. The DRS data obtained during metal deposition at RT and isochronous annealing were treated with the dynamic standard and restored standard methods, respectively.

### III. THE METHOD OF THE DYNAMIC STANDARD

To study film growth during metal deposition we used the method of dynamic standard (MDS). Unlike old method using curve $(\Delta R)/R(\lambda)$ to obtain optical properties of film [7], that one involves a dependence of DRC versus film thickness. The latter is immediate corollary from McIntyre-Aspnes formula (4) having been derived for thin and uniform films (i.e. its dielectric function $\epsilon_s$ does not depend on $h_{film}$). According to Eq. (4) the dependence of DRC versus film thickness $h_{film}$ being proportional to deposit coverage $h$ is linear. Therefore DRC of thin and uniform film is proportional $h$.

$$\frac{\Delta R}{R} = -8\pi \frac{h_{film}}{\lambda} \cdot \text{Im}\left(\frac{1 - \epsilon_s}{1 - \epsilon_b}\right) = kh.$$  

If film is not uniform or it is submonolayer, Eq. (2) should be used to calculate optical properties of film. Equation (2) does not contain variable $h$ obviously, although $\Delta \epsilon_{yy} = (\omega)$ being integral over averaged film thickness depends on $h$. This dependence is piecewise-linear function. For each deposit coverage region where $\Delta \epsilon_{yy} = (\omega)$ is linear the new standard can be chosen so that $\Delta \epsilon_{yy} = (\omega)$ becomes proportional to $h$. The proportionality coefficient does not depend on the standard. It contains information concerning change of dielectric function of film during its growth. Therefore we can rewrite Eq. (2) as

$$\Delta R = 8\pi \frac{h}{\lambda} \cdot \text{Im}\left(\frac{\Delta \epsilon_s}{1 - \epsilon_b}\right) = kh,$$

where $\Delta \epsilon_s = \Delta \epsilon_{yy}(\omega)/h$. It means that linear dependence DRC versus deposit coverage $h$ occurs during both uniform and sub-monolayer films growth. The latter has observed in [8]. Unfortunately the authors used obtained dependence to note a change of film growth mechanism and did not develop the idea into a new method.

Equation (5) is easy transformed to Eq. (4), if we assign $\Delta \epsilon_s = \epsilon_s - 1$. Therefore the formula (5) is universal expression and we’ll use it further. It should be used for experimental curve regions being proportional deposit coverage $h$ (1st region in Fig. 2(b) (upper)) to calculate $\Delta \epsilon_s$. If region is linear dependence versus $h$ (2nd region in the same figure), it should be converted in proportional...
one. We propose to use new standard for this region. The state of sample for deposit coverage \( h = h_0 \) is a good candidate in new standard because it is initial for the 2nd region. The calculated DRC value \( \Delta R/R^* \) is proportional to \( h^* = h - h_0 \) and so Eq. (5) can be used now. Asterisks sign the variables being used for new standard. If the curve consisted of 3 or more regions we should use one more new standard being chosen as described above and so on. During treatment experimental curve having several regions the standard being used for each single region is dynamically changed when moving to next region occurs. Therefore the idea and procedure being described above named the dynamic standard method. The old one, which we called the method of one standard (MOS), uses only one standard for all regions.

In order to obtain final expression being used for calculation of optical properties of films, Eq. (5) should be solved. It is equation with two unknown quantities, namely \( \Delta \epsilon_s^b \) and \( \Delta \epsilon_s^m \). It can be solved for 2 cases: 1) Involving 2nd equation being contained \( \Delta \epsilon_s^b \) and \( \Delta \epsilon_s^m \) (It must not be a linear combination of 1st one); 2) Eliminating either \( \Delta \epsilon_s^b \) or \( \Delta \epsilon_s^m \). The former is realized by using 2 polarization of light (s- and p- ones) instead of one being usually applied. The latter being simpler is usually used and we chose it. Provided the imaginary part of dielectric function of bulk Si \( \epsilon_s^{b} = 0 \), the value of \( \Delta \epsilon_s^b \) is easy eliminated. This condition takes place in spectral range investigated (up to 2.8 eV). The solution of equation is formula

\[
\Delta \epsilon_s^m = \frac{\lambda (\epsilon_s^b - 1) k}{8\pi},
\]

where \( \lambda \) - wave length, \( k \) - slope of experimental curve, \( \epsilon_s^b \) - real part of dielectric function of bulk Si and \( \Delta \epsilon_s^m \) - change of the imaginary part of dielectric function (CIPDF) of film. Typical \( \Delta \epsilon_s^m \) spectra are shown in Fig. 2(b) (lower). Usually they are linear combination of imaginary part of dielectric function of compounds being a components of film, and so

\[
\Delta \epsilon_s^m = \sum_{i=1}^{N} A_i \epsilon_i^{m},
\]

where \( N \)- quantity of composition to be in film and \( \epsilon_i^{m} \) - imaginary part of dielectric function of number \( i \) composition. The interpretation of coefficient \( A_i \) depends on its value. If it is positive then the coefficient \( A_i \) contains information about percentage of number \( i \) composition in growing film at the investigated stage of growth. The negative value suggests that composition is involved in reaction and its amount is decreased. Therefore the negative coefficient \( A_i \) is proportional to percentage of reacted number \( i \) composition in the dynamic standard. If values of \( \epsilon_i^{m} \) of all compositions being in film are known, the contribution of each composition may be estimated. More interesting object being search of film compound is often tried to solve. It is realized by resolving of CIPDF spectrum into those of the imaginary part of dielectric function (IPDF) of compounds.

To facilitate perception of mechanism of CIPDF spectrum formation the possible processes being occurred on surface and obtained values (DRC, CIPDF) during investigation of they by DRS are shown together in Fig. 2. During "C" atoms deposition 2 stages of "film" growth take place. The 1st stage is formation of "A" compound being resulted from "C" and Si atoms interaction (Fig. 2(a) (upper)). The CIPDF of this "film" resulted from reaction "C"+Si→"A" consists of IPDF of "A" and Si compounds:

\[
\Delta \epsilon_s^m = A_1 \epsilon_A^{m} + A_2 \epsilon_Si^{m},
\]

the value \( A_2 \) is negative due to the volume (thickness) of bulk Si reducing. In spite of the areas of Si and "A" compounds being equal, the inequality \( A_1 \neq |A_2 | \) takes place. It appears because of the volumes of used Si and grown compound "A" are different, the latter is bigger then the former. The difference volume is borrowed form vacuum, its IPDF equal zero for all photon energies. Equation (8) can be easy simplified provided \( \epsilon_Si^{m} = \epsilon_s^{b} = 0 \). This condition is true in investigated photon energy range and the expression looks like \( \Delta \epsilon_s^m = A_1 \epsilon_A^{m} \). Therefore CIPDF obtained for 1st region (blue curve in Fig. 2(b) (lower)) is proportional to IPDF of "A" silicide. This IPDF spectrum being inverse proportional to photon energy (in common case \( \Delta \epsilon_s^m \propto E^{-M} \), where \( M < 0 \)) suggests that "A" silicide is metal.

The 2nd stage is more complicated: two substances, namely "B" and "C" compounds, grow during "C" atoms deposition (Fig. 2(a) (lower)). The islands of "B" substance appear due to reaction "A"+"C"

\[
\rightarrow "B"
\]

and grow atop "A" crystallites, those of "C" one are bulk "C" metal crystallites (a priori "C" compound is metal) and located atop Si surface. Using Eq. (7) to describe CIPDF of "film" in the 2nd stage we obtain

\[
\Delta \epsilon_s^m = A_3 \epsilon_B^{m} + A_4 \epsilon_A^{m} + A_5 \epsilon_C^{m},
\]

the value \( A_4 \) is negative. The number of terms is 3 rather than 4 having been expected. It results from the bulk Si atoms are not involved in "C" islands formation. Therefore the term containing \( \epsilon_B^{m} \) is lacking in

FIG. 2: Illustration of RDE or molecule beam epitaxy (MBE) processes occurred in "C" metal-Si(111) system (a), dependence of DRC versus deposit coverage \( h \) obtained during investigation this system (b, upper) and calculated CIPDF of 'film' using MDS (b, lower).
FIG. 3: Illustration of SPE of 'C’ metal on Si(111) (a), dependence of reflection coefficient \( R \) on annealing time \( t \) for sample without- (b, upper) and with deposited substance ‘C’ film (b, center) and calculated VRF of annealed film using MRS (b, lower).

Eq. (9). It is worth adding in Eq. (9) when intense Si and "C" compound inter-diffusion occurs. The reaction "A"+"C”→“B" is similar to that for the 1st stage. Therefore the discussion of 1st stage can be used if substance "A" substitutes for Si. As \( \epsilon_A \neq 0 \), Eq. (9) is not possible to simplify in discussion and so CIPDF spectrum is linear combination of IPDF of these compounds (Fig. 2(b) (red)). This curve is superposition of 2 ones: the 1st curve being dependence \( \Delta \epsilon_{ss} \propto E^M \), where \( M < 0 \), is superposition of metal compounds "A" and "C" contributions, the former is negative; the 2nd curve contains 2-3 peaks and results from semiconductor compound "B" one. The surface phases located atop compounds give contributions too but they are by order of values lower than bulk films or crystallites ones. Therefore we do not take them, where possible, into account further.

IV. THE METHOD OF THE RESTORED STANDARD

Both described MDS and MOS are used to treat DRS data obtained during RDE [2, 3] or MBE [8, 9]. They can be used for initial stage of SPE (RT deposition, Fig. 3(a) (upper)) and are useless for other stages (increasing temperature and further annealing, Fig. 3(a) (center and lower)) being one technological operation. Though DRS studies of SPE have been made [10, 11], no methods for treatment obtained data were proposed. The main problem being arisen during elaboration of method is to find a convenient standard. The standard must meet the 2 requirements. The 1st one consists in equality of investigated sample and standard temperatures. It was supposed when Eqs. (2)-(4) have been derived [5, 6]. The calculated values being obtained applying this standard should be easy treated. It is the 2nd requirement. The 1st and 2nd stages of SPE are not used because conditions corresponding to them do not satisfy the 1st requirement. The 3rd stage remains only and its beginning can be used as standard having been used in [10, 11]. This standard has some drawbacks. The 2nd requirement is not satisfied being the 1st one. The standard is per se heated adsorbate film located atop substrate. Part of standard having been reacted gives a negative contribution in VRS being a characteristic of optical properties. Therefore VRS contains contribution of both annealed (reacted) film and standard. This VRS form is convenient for MBE or RDE being interested in dynamics of processes but it complicates interpretation of SPE data.

The 2nd drawback consists in search of appropriate time of transition from the 2nd to 3rd stages \( t_a \) (see Fig. 3(b) (center)). Its value depends on sample size and final temperature \( T_2 \). Therefore it should be chosen every time before experiments. If \( t >> t_a \), the reflection coefficient is appreciably changed due to temperature variation (Fig. 3(b) (upper and center)) and so the DRC value contains both film and temperature contributions. Therefore this choice is incorrect.

Having taken into account drawbacks of previous standard, we understood that no stages of SPE process could be used as standard for film annealing (the 3rd stage of SPE). Therefore we propose to use standards obtained in additional (preliminary) experiment being made before SPE one. The amount of standards equals that of values of temperature to be used in SPE experiment. It may be high, e.g. 7 in our work and 24!!! in [10]. In order to avoid confusion we propose the standard obtained in preliminary experiment at RT to be named as origin standard. Other standards are created by heating or, if any, cooling of it. There are two convenient candidates into origin standard. The 1st is Si substrate being covered native oxide prepared by Shiraki method and further outgassed at 500°C. Over candidate is clean Si sample after flashing at 1250°C. Though difference between reflection of the 2nd and 1st candidates is less than 1 percent for s-polarization [7], the clean Si is preferable to Si covered by native oxide due to its maximum work temperature being high. Therefore we used it as origin standard.

The preliminary experiment consists in registration of reflection of standards. The value of reflection coefficient \( R \) depends on temperature of the origin standard and so it is changed during heating. In order to choose value of reflection of the standard \( R_s \), the dependence of reflection \( R \) versus annealing time should be studied. It consists of 2 regions (Fig. 3(b) (upper)): sharp increasing of reflection coefficient (II stage) and saturation (III stage). The 1st stage takes place at RT when annealing time \( t = 0 \). This strange indexing of regions is chosen to emphasize similarity between this (preliminary) experiment and SPE one. The reflection coefficient of origin standard being averaged over the 3rd stage is regarded as that of the standard \( R_s \) at temperature \( T_2 \). By the way, the reflection of film during SPE experiment \( R_a \) is obtained using the same procedure (Fig. 3(b) (center)). To calculate DRC of film the values \( R_s \) and \( R_a \) should put in Eq. (1) as if...
they were obtained in one experiment. It means that the standard obtained in different (preliminary) experiment is restored in that one. Therefore the method being union of ideas and their realization described above is named as the method of restored standard (MRS).

Unlike MDS, MRS involves Eq. (2) rather than Eq. (5). It is convenient because it does not contain deposit coverage h being a sign of RDE or MBE processes. The expression (8) being an equation with two unknown quantities, namely \( \delta \Lambda''_y \) and \( \delta \Lambda''_y \), can be solved like Eq. (5) for two cases. The 2nd one is appropriate for our experiment conditions, i.e. \( \epsilon''_h = 0 \). The solution of equation is

\[
\delta \Lambda''_y = \frac{\Delta R \left( \epsilon''_h - 1 \right)}{R_{exp} \lambda} \frac{8\pi}{}, \tag{10}
\]

where \( \lambda \)- wave length, \( \epsilon''_h \)- real part of dielectric function of bulk Si and \( \delta \Lambda''_y \)- VRF of film. Typical \( \delta \Lambda''_y \) spectrum is presented in Fig. 3(b) (lower). Unlike CIPDF characterizing film formation dynamics during RDE and SPE, VRF describes optical properties of certain composition film grown during SPE. It is a linear combination of IPDF of compounds being a components of film

\[
\delta \Lambda''_y = \sum_{i=1}^{N} \theta_i h_i \epsilon''_i, \tag{11}
\]

where \( N \)- quantity of composition to be in film, \( \epsilon''_i \)- IPDF of number \( i \) composition, \( h_i \) and \( \theta_i \)- its thickness and percentage of its area in film, respectively. When material of standard (bulk Si) is involved in reaction, the term containing its IPDF is negative. If values of \( \epsilon''_i \) of all compositions being in film are known, the effective thickness \( \theta_i h_i \) of each composition may be estimated. The inverse object being search of film compound when \( h_i \) and \( \theta_i \) are obtained by STM or AFM is more complicated because it means resolving of VRF spectrum into those of IPDF of compounds. If this spectrum contains some resolvable peaks, this object can be easy solved.

Using Eq. (11) for the case shown in Fig. 3(a) (lower) finalizes the description of MRS. In this case

\[
\delta \Lambda''_y = \Theta(h_2 + h_3)\epsilon''_A + (1 - \Theta)h_1 \epsilon''_C - \Theta h_3 \epsilon''_b. \tag{12}
\]

The thickness of compound "A" film was resolved into two terms to emphasize involving of bulk Si in reaction. Therefore the last term is negative and contains \( \Theta \) rather than one, compound "C" were grown atop bulk Si without involving. If VRS spectrum described by Eq. (12) is presented in Fig. 3(b) (lower), three peaks are contribution of semiconductor silicide "A" and background like \( \delta \Lambda''_y \propto E^M \), where \( M < 0 \), appears due to metal compound "C" one.

V. RESULTS AND DISCUSSION

The method of SPE is known to consist of two stages: the deposition of atoms on substrate at RT (or low temperatures) and further annealing at elevated one. The final state of film depends on its initial composition having before annealing. Therefore the study of 1st stage of

FIG. 4: Fe/Si(111) at RT: a) The dependencies \( \Delta R/R \) versus Fe thickness for some energies, b) The dependence of CIPDF \( \Delta \epsilon''_h \) versus photon energy.

SPE was done in detail. Unlike this stage having been studied by MDS, the optical properties of film obtained at last stage have been investigated by MRS and follow those of initial one.

A. SPE of iron on Si(111)

The results of DRS study of iron deposition on Si(111) at RT are shown in Figs. 4(a)(b). The former contains dependence of DRC versus deposit iron thickness \( h \) for certain photon energies. Their values are chosen variation of DRC to possess a high value so that the variation of curve slope can be easily distinguished. To determine flex points we always use dependence of DRC derivative \( (\Delta R/R) \) on \( h \). A region of maximum derivative change corresponds to flex point vicinity. We found the only flex point and its value being a boundary between regions is 0.18 nm. To verify the obtained value we calculated line equation coefficients (\( k \), \( b \)) and plotted lines for I and II regions (red and blue ones) at 2.0869 eV (Fig.4 (a)). These lines are good fitting of the experimental curve and
coincide with polynomial fitting marked by black curve in certain regions. The cross point of the lines is close to obtained flex point. These results are very good corroboration of correctness of obtained boundary. Other boundaries are difficult to find using this experimental data and so they are marked by dotted lines. The value of CIPDF depends on their positions. Therefore search of them is important problem being solved in MDS. The missing information is obtained from another experiment involving either DRS or other techniques.

In our case other UHV chamber equipped with LEED was used. The experiment consist in Fe certain portions deposition on Si(111) at RT being followed LEED study to obtain LEED patterns for all investigated coverage \( h \). After deposition of the 1st portion having been 0.025 nm, (1 \( \times \) 1) pattern was observed only. Further portions deposition did not result in changing of LEED pattern being (1 \( \times \) 1) until iron coverage equals 0.44 nm. When it transcedes this value, sharp decrease of spot intensity occurs. It results from bulk iron crystallites formation. Therefore the value 0.44 nm is assumed to be right boundary of the 2nd region. The (7 \( \times \) 7) LEED pattern is known to correspond with initial stage of RT iron deposition [12]. Therefore iron coverage of 0.025 nm film having (1 \( \times \) 1) periodicity may be used as left boundary of the 1st region.

The mentioned above regions (0.025-0.18 nm and 0.18-0.44 nm) are linear. The spectra of CIPDF calculated for those regions presented in Fig.4 (b). They are similar: 1) The number of peaks (five: A-E peaks) is equal in spectra, 2) The positions of four peaks are not changed and that of B one is negligible, 3) The metallic nature of dependence CIPDF versus photon energy in near IR (1.1-1.7 eV) is observed in spectra, 4) They contain a broad peak at 2.1 eV, its position is slightly changed, 5) The hollow containing peak D is special feature of spectrum. Therefore the processes occurring at the 1st and 2nd stages (1st and 2nd regions) are analogous and films composition is similar. It suggests the formation of crystallites (islands) atop bulk Si and continuous crystallites (islands) film for the 1st and 2nd regions, respectively.

To find composition of crystallites (islands) the 1st or the 2nd spectra should be studied in detail. We chose the former for analyzing. As spectrum contains metallic contribution, let us compare it with those of metallic silicides obtained in previous papers [2, 13]. The investigated spectrum and that of FeSi in [2] are similar. They contain the following common features: 1) Dependence of CIPDF (IPDF) versus photon energy is abrupt in near IR (1.1-1.7 eV), 2) Two peaks, namely A and the broad ones, are observed in spectra, their position are 1.5 and 2.2 eV. The mean position between B and C peaks is used as that of broad peak. Those features were also found for single-crystal FeSi [13]. Therefore studied CIPDF spectrum contains mainly FeSi contribution.

However there is discrepancy between it and obtained in [2] one. It is formulated in following items: 1) Dependence of CIPDF versus photon energy in near IR for our experiment is more abrupt than IPDF one for FeSi in [2], 2) the broad peak obtained in this investigation is higher than that in [2]. The latter suggests that degree of perfection of FeSi crystallites obtained in this work and in [2] is different. To determine this value theoretical spectra of ideal FeSi single-crystal obtained by band calculation [13] should be compared with experimental ones. In theoretical spectrum the heights of broad peak and A one are comparable. Therefore the degree of perfection of FeSi crystallites grown during the 1st stage is higher than those obtained in [2]. This value depends on number of additional atoms (Si or Fe) in ideal FeSi crystallite (crystal), the higher number of additional atoms, the low degree of perfection. It can be estimated by analyzing shape of spectrum. This question will be discussed below.

Furthermore all peaks observed in Fig.4 (b) are easy to find in theoretical one and so they can be attributed to transitions in FeSi crystallites. However they are missing in experimental spectrum obtained in this work. This surprising fact may be resulted from low resolution of applied wide energy range optical device. There is a following correlation between resolution and photon energy range: the higher the latter, the lower the former. Therefore four peaks (B-C peaks) were unresolved.

Next discrepancy (1st item) should be scrutinized because it contains useful information. The study of this feature touches other one (hollow at 2.5 eV). The positions of hollows are 1.7 and 2.5 eV, respectively. They are appeared due to involving bulk Si in reaction and result in steepness increasing of both left and right slopes. As IPDF of bulk Si is zero in investigated photon energy range, it does not give negative contribution in CIPDF. Other candidate is Si - FeSi interface having low energy (up to 3.0 eV) states. It can reduce CIPDF when it is changed. To confirm this assumption the investigations of interface changing during atoms deposition were adverted [7-9]. The results of two of them [8, 9] are unsuitable for our case. The former contains results of investigation of unreactive Ag-Si(111) interface. The word "unreactive" suggests that silicide is not formed in this system. Therefore the results presented in [8] cannot be applied in our work.

Article [9] is about hydrogen adsorption on Si(111)/7 \times 7 at RT. The described results are very useful for alkali elements-Si(111) system study. However, hydrogen atom can saturate the only dangling bond, and it cannot occupy bridge site (saturate two bonds). We paid attention to this question because in silicide crystallites iron occupies exactly bridge site. Therefore we fail to use paper [9]. Article [7] is devoted to study of oxygen adsorption on Si(111) at RT. This element has not mentioned above drawback and so we applied the results presented in [7]. The peak positions obtained in this paper (1.8 and 2.5 eV) and our values (1.7 and 2.5 eV) are comparable. Therefore assumption concerning influence of Si-FeSi interface changes on CIPDF proposed above deserves attention.

Having studied of the 1st spectrum in detailed proceeds with the next one paying attention to distinctions. The CIPDF value is lower than that for the 1st stage in wide energy range (up to 2.4 eV). This changing of CIPDF is usually observed when continuous film has just been formed [2]. In our case it occurs at thickness of 0.18 nm. This phenomenon is accounted for different surface being a foundation for crystallite: it is (1 \( \times \) 1) Si surface and FeSi continuous film one in the 1st and 2nd stages, respectively. In the 1st stage FeSi-Si interface is formed during crystallites growing and give additional positive contribution in CIPDF. In the 2nd stage crystallite height increasing occurs but interface area does not change.
FIG. 5: AFM picture of finale state of iron film: a) After RT deposition, b) After annealing at T=600°C.

facto. Therefore it does not contribute in CIPDF and its value is reduced. On the other hand, when film becomes continuous the crystallites growth conditions are changed. The Si atoms having easy defused on silicon surface in the 1st stage reduce their velocity in the 2nd one because they must arrive atop before defusing on film surface. Coefficient of atoms diffusion on this surface is low due to film relief. Therefore growth of crystallites slows down. The superfluous iron atoms are resolved in FeSi crystallites and change their optical properties (IPDF).

In our previous work [14] the increasing of interface electron concentration during RT iron deposition on Si(111) was found. When iron coverage is not high (up to 0.025 nm) this phenomenon is accounted for appearance of additional surface level located in band gap. If iron coverage is higher than 0.18 nm, the film becomes continuous and current flows along both the substrate and the film. In this case two layers model can be applied for calculation concentration and mobility of carries. The reason of electron concentration increasing for intermediate case (0.025-0.18 nm) we could not find than, i.e. in [14]. Our DRS experiments give additional information concerning film formation: the FeSi bulk crystallites growth occurs when iron coverage increasing from 0.025 nm to 0.18 nm. Therefore in this case the concept of phenomenon should be based on local metal-semiconductor contact model. It is known that the concentration of carries in contact area depends on work function of both metal and semiconductor. If work function of metal is lower than that of semiconductor, the electron concentration is increased in semiconductor and vice verse. Therefore the increasing of electron concentration implies that work function of FeSi (metallic silicide) is lower than that of semiconductor. For p-doped Si it results in metal-semiconductor barrier (Shottky barrier) being lower than Si bandgap. Therefore the located atop metallic silicide FeSi can reduce the effective bandgap and so the red edge (minimum photon energy) is moved towards low energies. During iron deposition the finish Shottky-diode is created locally without making any efforts at RT. Applying of this diode in CCD devices can result in increasing of used photon energy range.

Let us revert to discussion of our results. The film composition is known and so we can begin analyzing of data obtained at elevated temperatures. They are shown in Fig. 6. The annealing at temperatures lower than 350°C does not result in changing of VRF spectra shape. It suggests that degree of perfection of FeSi crystallites grown at RT is high and so their composition is not appreciably changed. The comparison of spectra obtained at 350°C and at 300°C reveals the following negligible changes: 1) The value of VRF is increased in near IR (up to 1.7 eV), 2) The height of broad peak is reduced. The only reasonable explanation of those changes is to assume involving additional iron atoms having been resolved in FeSi crystallites during RT deposition into silicide formation reaction. The rule linking changes of VRF spectrum and crystallite composition is formulated as follows, the lower broad peak at 2.2 eV, the more Si atoms resolved in crystallite. Other formulation of the rule - the higher value of VRF in near IR, the more Si atoms resolved in crystallite. These rules are correct for metallic iron silicides and bulk Fe. Unlike they having cubic lattice, the semiconductor one has orthorhombic lattice. It does not obey the rule.

Let us apply the rule for FeSi grown in [2] to estimate composition of its crystallites. The result obtained by using the rule is unexpected: the film contains a lot of additional Si atoms, i.e. high deposition rate causes increasing of number of Si atoms in silicide film. To find a reason of this unexpected result the behavior of Fe atoms on substrate should be scrutinized. After arriving on surface iron begins to diffuse either atop surface or into bulk material. Other iron atoms located around influence on

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its diffusion: the less their amount, the higher probability of bulk diffusion and further silicide formation. Increasing of deposition rate results in bulk iron formation. As a number of Fe atoms diffusing into bulk Si is not enough, the amount of Si atoms resolved in silicide crystallites is high. If FeSi film obtained in [2] had been annealed at 350°C, the shape of its VRF spectrum would have been changed considerably.

LEED study of film annealed at 300°C and 350°C confirms assumption stated above, the (1 × 1) periodicity is not changed. Other LEED pattern, namely (2 × 2) one, appears when annealing temperature achieves 400°C. It was not modified even after having been annealed at 600°C. These results are confirmed with obtained ones in [16]. According to this paper the temperature of (2 × 2) pattern appearance depends on deposit Fe coverage: the more coverage, the lower temperature. For our value of coverage it takes value between 350 and 400°C. Temperature of (7 × 7) pattern appearance does not depend on coverage and equals 730°C. The AES peak ratio (Fe/Si) is decreasing at all temperatures. It suggests that Si atoms concentration in film is increased. These features have to influence on VRF spectrum at 400°C and they indeed do. The shape of spectrum is appreciably changed (Fig. 6(a)). The value of VRF is increased in near IR, height of the broad peak is reduced. It means that concentration of Si atoms in FeSi is increased. The positions of four peaks, namely A-D, and their height are changed. The latter is presented in Table I. It also contains experimental ones obtained in [2] and theoretical values [15]. The moving of peaks suggests either formation of new silicide(s) or changing of growth mechanism of old one(s) occurs. If noticeable changes in VRF, like our case, are observed, the former should be supposed; otherwise the latter is preferable. The number of new compounds is two at least: metallic and semiconductor FeSi$_2$ silicides, the latter is β-FeSi$_2$. Both the former and the latter use FeSi crystallites for their formation. The study of FeSi→β-FeSi$_2$ transition has been performed in [2], it also contains the scheme of this transformation. The FeSi, α-

FeSi$_2$ and γ-FeSi$_2$ metal silicides cells are presented in [17]. They have cubic cells and so FeSi→α-FeSi$_2$ and FeSi→γ-FeSi$_2$ transitions are easy realized be insertion additional Si atoms. We have not any information about optical properties of α-FeSi$_2$ and γ-FeSi$_2$ silicides. Therefore we cannot answer the following questions: 1) How many silicides were formed, 2) What metallic silicides are grown. However we keep the experimentally obtained results in mind and find method of pure silicides formation in UHV condition.

The values of VRF of annealed at 450°C film are increased in wide photon energy range (1.4-2.8 eV) and are solely positive. This striking result occurs only at this temperature. The peaks A, C, E are noticeably moved, their height are increased. The D peak is increased too but its position is not changed. The peak positions are coincided with those of β-FeSi$_2$(010) and β-FeSi$_2$(001). If VRF spectrum obtain at 450°C compares with that at 400°C, one can find that positions of certain peaks are changed: B, C, D - for 400°C and A, C, E - for 450°C. The former is β-FeSi$_2$(010) peaks and the latter - β-FeSi$_2$(001) ones. It suggests that preferred formation of β-FeSi$_2$(010) at 400°C and β-FeSi$_2$(001) at 450°C, respectively, occurs. The peak C is common for both orientations. Therefore it must be higher than those of other ones at 450°C, if this assumption is correct. This peak is indeed higher.

The annealing of film at 500°C (Fig. 6(b)) results in reducing of VRF in used photon energy range. Although peaks positions are negligibly shifted, their height is distinctly reduced. Two hollows appear. These features imply that film was cracked during annealing. It consists of large islands separated by bulk Si. The FeSi$_2$-Si interface is disappeared where split runs. Therefore it gives a negative contribution especially at 1.7 and 2.5 eV as discussed above. If cracked film is annealed at 550°C, islands area is reduced and their height is increased. Therefore VRF is increased too at wide region, except close to 1.7 and 2.5 eV ones. The peaks are moved to positions of β-FeSi$_2$(001) ones. It means that certain plate of β-FeSi$_2$ growth occurs. These tendencies are observed at the last spectrum obtained at 600°C. The morphology of film, as

| $T_{fim},$ °C | A | B | C | D | E |
|-------------|---|---|---|---|---|
| 20 (1st stage) | 1.4433 | 2.1008 | 2.2608 | 2.5220 | 2.7257 |
| 20 (2nd stage) | 1.4524 | 2.1174 | 2.2617 | 2.5084 | 2.7155 |
| 300 | 1.4524 | 2.1076 | 2.2626 | 2.5020 | 2.7059 |
| 350 | 1.4524 | 2.1106 | 2.2681 | 2.5020 | 2.7059 |
| 400 | 1.4660 | 2.0720 | 2.2843 | 2.4819 | 2.7007 |
| 450 | 1.5047 | 2.0810 | 2.3331 | 2.4770 | 2.6904 |
| 500 | 1.5195 | 2.0929 | 2.3322 | 2.4924 | 2.7272 |
| 550 | 1.4922 | 2.0849 | 2.3084 | 2.4880 | 2.7213 |
| 600 | 1.4581 | 2.0849 | 2.2951 | 2.5161 | 2.7213 |

Transitions in β-FeSi$_2$ (1st stage) [2]

| Planes | Transitions in bulk β-FeSi$_2$ [15] |
|--------|----------------------------------|
| (001) | 1.40 | 1.50 | 1.90 | 2.10 | 2.30 | 2.50 | 2.70 |
| (010) | 1.40 | 1.70 | 2.10 | 2.30 | 2.50 | 2.70 | 2.90 |
| (100) | 1.10 | 1.50 | 1.90 | 2.30 | 2.50 | 2.70 | 2.90 |

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expected, is rough (Fig. 5(b)): the high crystallites follow flat terraces. To find number of types of island on surface we usually calculate aspect ration. This operation we used for all presented AFM images. The histogram plotted for Fig. 5(b) contained two maximum: 1 and 1.3. The former means quadratic islands, the latter implies rectangle ones. It means that two iron silicides are on the surface. One type of island is semiconductor silicide crystallite, another is metallic one. The formation of bulk iron crystallites having quadratic shape (aspect ration 1) is improbable process at this temperature. Therefore we suggest that this value of aspect ratio is corresponded to one of the mentioned above iron metallic silicides. The second value of aspect ratio is close to that for bulk β-FeSi$_2$ crystallites. Thus final film contains metallic and semiconductor (β-FeSi$_2$) silicides. It is not continuous. To grow continuous film, it should be annealed at 450°C. This value depends on deposit coverage: the more coverage, the lower temperature, as discussed above.

B. SPE of chromium on Si(111)

The results of DRS study of chromium deposition on Si(111) at RT are shown in Figs. 7(a)(b). The former contains dependence of DRC versus deposit iron thickness h for certain photon energies. Three flex points, namely 0.025, 0.043 and 0.091 nm, may be clear observed and their values are a boundary between regions. The last (right) boundary is difficult to find using this experimental data and so it is marked by dotted line. The size of regions and boundaries position are coincided with those obtained in [14]. According these results the processes having started at 0.1 nm is not finished at 0.3 nm (the increasing of Hall voltage is not stopped). Therefore "dashed" boundary (at 0.26 nm) belongs last stage and CIPDF calculated for this stage is correct.

All regions (0-0.025 nm, 0.025-0.043 nm, 0.043-0.091 nm and 0.091-0.26 nm) are linear. The spectra of CIPDF calculated for those regions presented in Fig. 7(b). They are different. It implies the processes occurring at stages are different, too. The first region range for chromium deposition is coincided with that for iron one. It suggests the formation of Cr-Si interface resembles that of Fe-Si one at the 1st stage, i.e. destruction of 7 × 7 reconstruction oc-
FIG. 8: VRF spectra of chromium film obtained after 15 min annealing: a) T = 350-500°C, b) T = 550-650°C.

The CIPDF spectra obtained at the 2nd stage looks like semiconductor silicide one [18] and so the formation CrSi₂-like compound is supposed to occur. At the 3rd stage metallic crystallites are grown predominantly, although CrSi₂-like ones growth does not stop. The former may be both metallic silicide (CrSi or Cr₃Si) and bulk Cr. To find the composition of metallic crystallites we compare peaks positions with energies of possible transitions obtained by analyzing DOS of these candidates [19]. The CrSi and bulk Cr crystallites formation is probable, the former is more plausible. At last stage the processes are not changed and CrSi and CrSi₂ islands growth occurs, the latter contribution is increased. AFM image of morphology of final film is shown in Fig. 9(a). The surface of sample is very rough, the depth of hollow varies from 0.5 to 1.8 nm. It suggests that high Si atom transport occurs at RT. This behavior of Si atoms is accounted for silicide formation. All islands located atop surface can be separated in two groups: triangle-like and rectangle-like crystallites. It implies the growth of two silicides. The latter is found also after annealing at 650°C (Fig. 9(b)). Therefore rectangle-like crystallites are CrSi₂ ones and triangle-like islands are CrSi crystallites.

The annealing at 350°C result in significant changing of VRF spectrum shape (Fig. 8(a)). It differs from CIPDF spectrum obtained at the 4th stage. It suggests that film composition is appreciably changed during annealing. It is interesting that shape of VRF spectrum and CIPDF one obtained for the 3rd region are similar. Destruction of CrSi₂ crystallites and further bulk Fe ones formation are improbable processes at this temperature. Therefore CrSi islands growth should be assumed at 350°C and RT. The change of spectrum shape and value of VRF are observed at 400°C. Bulk CrSi₂ crystal peaks appear. It suggests that CrSi → CrSi₂ transition occurs. Increasing of annealing temperature results in increasing of VRF value, although spectrum shape is negligible changed. VRF achieves maximum value at 500°C (Fig. 8(a)) and then it is reduced (Fig. 8(b)). During increasing, all peaks noticeably shifted, implying considerable changing of film composition. We suppose that film contains only semiconductor silicide (CrSi₂) after annealing at 500°C. Reducing of CIPDF of the film annealed at 550°C arises from film cracking and further coalescence of crystallites belonging to islands during annealing. The splits are distinctly observed in AFM picture of final state

FIG. 9: AFM picture of final state of chromium film: a) After RT deposition, b) After annealing at T = 650°C.
of film (after annealing at 650°C) (Fig. 9). The coalescence of CrSi$_2$ crystallites occurring at these temperatures is also presented in this picture. These results are conformed to phase diagram obtained in [20], although the discussed above result concerning reducing of VRF was misinterpreted in this paper.

VI. CONCLUSIONS

The SPE in Fe-Si(111) and Cr-Si(111) systems was first studied by DRS. It was found that iron deposition rate affects on concentration of Si atoms resolved in FeSi: the higher rate, the more concentration. If deposition rate is about 0.016 nm/min, the degree of perfection of FeSi crystallites is high. It was noticeable decreased when rate was 3 times higher. During RT Cr deposition investigation four stages of growth was observed (0-0.025 nm, 0.025-0.043 nm, 0.043-0.091 nm, and 0.091-0.26 nm). The 1st is known 7 × 7 reconstruction destruction, other ones - CrSi and CrSi$_2$-like silicide formation. To grow continuous CrSi$_2$ film, it should be annealed at 500°C. If the aim is to obtain continuous FeSi$_2$ film, you anneal it at 450°C. These values depend on deposit coverage: the more coverage, the lower temperature. Therefore they should be found experimentally for certain coverage.

Acknowledgments

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