Effect of chemical ordering on optical properties of Fe_3Si epitaxial films

Ivan Tarasov[1,*], *Zakhar* Popov[2], *Maxim* Visotin[1,3], *Ivan* Yakovlev[1] and *Sergey* Varnakov[1]

[1]Federal Research Center KSC Siberian Branch Russian Academy of Sciences, 660036 Krasnoyarsk, Russia
[2]The National University of Science and Technology MISiS, 11999, Moscow, Russia
[3]Siberian Federal University, 660041 Krasnoyarsk, Russia

Abstract. Optical characteristics (electron energy loss function, optical conductivity σ, permittivity ε, refractive index n, extinction coefficient k, and absorption coefficient α) of a 30 nm thick epitaxial Fe_3Si iron silicide films grown at different silicon substrate temperature (26, 100, 200, 300 ˚C) were determined within E = 0.74–6.46 eV photon energy range using spectroscopic ellipsometry technique. The experimental data are compared to the optical characteristics calculated in the framework of the density functional theory using the GGA–PBE approximation. Variations of the optical characteristics spectra are discussed from the point of view of chemical ordering of DO3 type crystal structure. It is asserted that the electron energy-loss function, optical conductivity and extinction coefficient of the Fe_3Si iron silicide films undergo noticeable changes in different spectral ranges over the whole spectrum between 0.74 and 6.46 eV due to variation in the chemical order. Information on the effect of chemical ordering on the optical properties obtained here allows one to carry out quick qualitative analysis of Fe_3Si film crystal quality during the synthesis procedures by ellipsometry method in situ.

1 Introduction

Epitaxial thin films of iron silicide Fe_3Si grown on semiconducting substrates, along with other Heusler compounds [1] attract a lot of attention on account of their possible application in spintronics devices where effective injection of spin-polarised current into a semiconductor and its detection is essential. Except for their potential application as spin injectors, these materials are interesting in the other field of applied physics. Since they possess excellent soft magnetic properties, small values of the width of the ferromagnetic resonance line and the coercive field, high permeability and saturation magnetisation, while having a higher resistivity for lower eddy losses, they might be used in different electrically controlled devices of the microwave range. Larger magnetooptical Kerr effect (MOKE), and higher spin polarisation degree in comparison with pure bcc-Fe make this Heusler compound a prominent candidate for fabrication of ferromagnetic periodic structures such as magnetophotonic crystals. However, the optical properties of such films were poorly investigated whereas this information could make easier understanding of the situation with enhancement of magnetooptical response of iron-rich Fe-Si alloy thin film. From another point of view, deeper understanding interrelationship between optical and structural, electronic properties and defect formation of epitaxial Fe_3Si alloys thin films would bring us a quick tool for estimating the quality of as-grown or being grown thin films by in situ or ex situ optical methods, such as ellipsometry.

2 Experiment and calculations

2.1 Sample preparation

Five epitaxial $Fe_3Si(111)$ thin films (denoted FS1-4 and FSC) on silicon substrate Si(111) were prepared according to the following technological procedures. The experiment was carried out with ultrahigh vacuum molecular beam epitaxy "Angara" set-up equipped with a system of reflection high-energy electron diffraction (RHEED) and a one-wave ellipsometer. The base pressure in the growth chamber was 6.5×10^{-8} Pa. Silicon substrates with 1.0 º Si(111) plane miscut were used. The substrates were prepared by the special chemical treatment in air and a thermal flashing at 900 °C in vacuum.

The Fe_3Si films were prepared by molecular-beam epitaxy (MBE) technique with simultaneous deposition of Si and Fe on Si(111) 7×7 substrate at room temperature for the FS1 sample and heated at 100, 200, and 300 °C for the FS2, FS3 and FS4 samples. The substrate temperature in the case of the FSC sample was 200 °C. Deposition rates were Fe – 1.24 nm/min, Si – 0.88 nm/min. The component materials were evaporated from Knudsen effusion cells. The film thickness estimated by laser ellipsometry technique was about 30 nm. FSC sample was obtained to carry out structural characterisation by X-ray diffraction analysis (XRD). In order to obtain symmetrical scan with well distinguishable reflections, the thickness of the FSC sample was increased up to 70 nm. The films were deposited at the oblique incidence angle, so-called the oblique sputtering.

* Corresponding author: tia@iph.krasn.ru

The angle between the Fe flow direction and the normal to the substrate surface was 14º. XRD analysis was performed on a PANalytical X'Pert PRO diffractometer equipped with a solid state detector PIXcel on Cu and Co Kα radiation. The ellipsometric spectra were measured with help of VASE J.A. Woollam ellipsometer in unique scientific installation (USI) "Physics, Chemistry, and Mechanics of Crystals and Thin Films" in Institute of problems of mechanical engineering Russian Academy of Sciences (IPME RAS), St. Petersburg, Russia.

2.2 DFT calculation of optical properties

The electronic and geometric structures of DO3 type Fe_3Si silicide were calculated by quantum chemistry simulations based on the licensed program package VASP 5.3 [2] in the framework of the density functional theory (DFT) using the plane wave basis and the projector augmented wave (PAW) formalism. To describe the exchange-correlation functional, we use the generalised gradient approximation (GGA) involving also the Perdew–Burke–Ernzerhof (PBE) approximation. For optimisation of the unit cell geometry of Fe_3Si (Fm3m), the first Brillouin zone in the reciprocal space is automatically divided into a 6 × 6 × 6 mesh chosen according to the Monkhorst–Pack scheme. In the calculations, the cutoff energy E_{cutoff} is equal to 293 eV. In the modelling of the structure under study, the optimisation of the geometry is performed up to maximum values of the forces acting on atoms and equal to 0.01 eV/A. After calculation of the ground state by the VASP program, we calculate the frequency dependent dielectric matrix. The details of this method are described in [3]. In order to illuminate how the chemical disorder in ideal DO3 crystal structures of the Fe_3Si compound can affect the optical characteristics the ideal DO3 (Fig.1a) and with a particular chemical disorder (Fig1b) Fe_3Si unit cells were used for calculations.

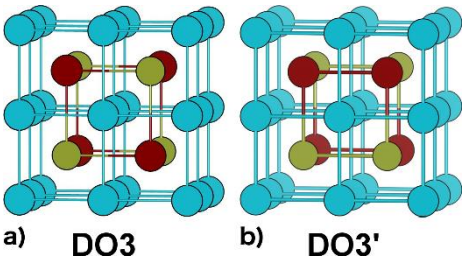

Fig. 1. (a) Ideal DO3 crystal structure of Fe_3Si (a) compared to a disordered DO3 (b). Red, blue spheres represent Fe, green – Si.

3 Results and discussion

3.1 XRD analysis

The in-plane epitaxial orientation was analysed using the asymmetrical φ-scans of reflections {224} from the Fe_3Si iron silicide film and Si substrate. Typical φ-scan for the FSC sample (Fig. 2b) reveals the following orientation relationship: $Fe_3Si(111)[1\text{-}21] \parallel Si(111)[11\text{-}2]$. The lattice parameter of ordered DO3 (Fm3m) and disordered B2 (Pm3m) and A2 (Im3m) type crystal structures is strongly dependent on silicon content. For the crystal structure analysis, a series of characteristic reflections 111, 222, 333 and 444 from the Fe_3Si film (FSC sample) were measured (Fig. 2(a)). To reduce the 111 reflection from the Si substrate, an additional tilt of 1° was applied. The cubic (Fm3m, DO3 type) lattice parameter a = 5.666(1) Å was determined from the XRD pattern by the derivative difference minimization method [4] and corresponds to stoichiometric Fe_3Si compound, with chemical composition Fe (75 at. %) and Si (25 at. %) [5]. The silicon content of the $Fe_{1-x}Si_x$ alloy films was calculated by estimation of specific volume for one silicon atom in the $Fe_{1-x}Si_x$ unit cell.

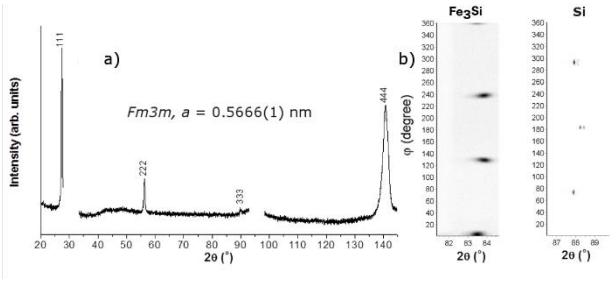

Fig. 2. Observed XRD patterns for 4 characteristic diffraction peaks of Fe_3Si (a). 2D-images for φ-scans of reflections {224} from Fe_3Si film and Si-substrate (b).

3.2 Optical characteristics

One could expect that in metallic compounds such as stoichiometric Fe_3Si iron silicide effect of chemical disorder on optical properties would be negligible. Nevertheless, that scarce data on optical properties of Fe-rich Fe-Si alloys, which exist in the literature available [6,7] suggests that changes in optical characteristics caused by thermal annealing can result from DO3-B2-A2 transformations. It is known that optical conductivity is most sensitive and informative spectral parameter characterising the frequency dependence and the intensity of the optical response of the medium [8]. However, a survey of other optical parameters characterising the optical response of the Fe_3Si compound seems to be essential to define which optical parameter could be easily used for qualitative controlling chemical ordering by optical methods. In the section information about real and imaginary parts of permittivity, refractive index n and extinction coefficient k, electron energy loss function, absorption coefficient α, optical conductivity σ and reflectivity R is given. All optical characteristics were calculated using real and imaginary parts of permittivity obtained by converting ellipsometric parameters with the semi-infinitive medium model. Reflectance from the interface Fe_3Si/Si is not considered and expected to give a small contribution due to high absorbance of the Fe_3Si compound. Nevertheless, more complex optical models will be considered in the nearest future.

3.2.1 Permittivity

Overlook of spectral dependence of experimental and calculated permittivity (Fig.3) demonstrates their qualitative

accordance. Real part of permittivity has values in the range between 2-6.46 eV typical for metals and is caused by both commensurable impact of free-carrier absorption and bound electrons. At lower photon energies, < 2 eV, impact of bounded *d*-electrons increases and becomes prevailing. Further decrease of Real(ε) with lowering photon energy is expected due to intraband acceleration of free-carries by electromagnetic field. Comparing to metals with high concentration of free electrons Fe_3Si compound demonstrates high impact of interband transition at energies about 1 eV, which mainly caused by transitions from flat bands formed by d_{xy}, d_{xz}, and d_{yz} (T_{2g}) to those ones created by d_{z2} and d_{x2-y2} states (E_g) [9]. Effect of synthesis temperature is negligible over the whole spectral range and mainly can be easily noticed in imaginary part of permittivity at photon energies about 1 eV due change of Im(ε) value from 45 up to 55 and slight shift of the peak position. Consideration of the specific chemical disorder in Fe_3Si compound (Fig. 1) reveals a possible reason for shifting of low energy prominent absorption peak, from ~1.8 to ~1.3 eV.

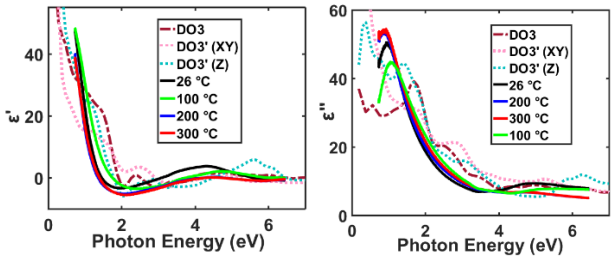

Fig. 3. Real (left) and imaginary (right) part of permittivity of Fe_3Si thin films obtained at different temperatures of Si substrate (solid lines) along with ab initio calculation (dashed lines)

3.2.2 Refractive index and Extinction coefficient

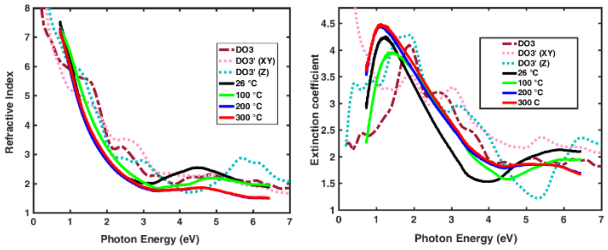

Fig. 4. Refractive index (left) and extinction coefficient (right) of Fe_3Si thin films obtained at different temperatures of Si substrate (solid lines) along with ab initio calculation (dashed lines)

In turn, refractive index and extinction coefficient spectra (Fig. 4) are more sensitive to the synthesis temperature and chemical disordering than permittivity spectra. One can readily note prominent difference between spectra corresponded to Fe_3Si films obtained at room temperature (RT), 100 °C and 200, 300 °C. The spectra referred to the 200, 300 °C synthesis temperatures are in almost full coincidence, which could be evidence of termination atom interdiffusion between different Wyckoff position in Fe_3Si unit cell. Another noticeable feature of the extinction spectrum is a profound minimum close to 4 eV for RT-grown sample and 4.5 eV for 100°C. As theoretical curve for disordered Fe_3Si unit cell shows the chemical disordering can result in such shifts. The photon energy value of the minimum location is about 5.3 eV.

3.2.3 Electron energy loss function (ELF)

The electron energy-loss function (ELF) describes the interaction by which energy is lost by a fast moving electron travelling throughout the material. Interactions may include phonon excitation, interband and intraband transitions, plasmon excitations, inner shell ionisations and Cerenkov radiations [10]. As it can be seen, photon energy dependence of ELF has one distinctive feature, a broad peak around 3.5 eV, which is sensitive to chemical order according to the theoretical curves (Fig. 5).

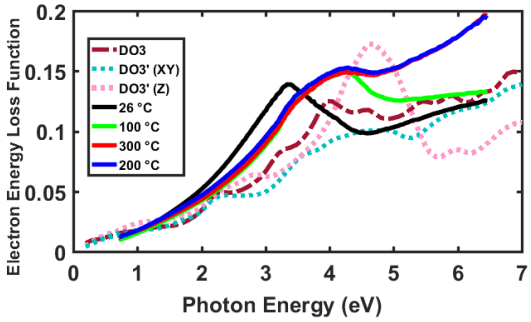

Fig. 5. Electron energy-loss function of Fe_3Si thin films obtained at different temperatures of Si substrate (solid lines) along with ab initio calculation (dashed lines)

The synthesis temperature strongly affects ELF. Thus, RT results in formation an abrupt prominent peak with position at ~3.2 eV, whereas increasing temperature up to 100 °C causes its shift to higher energy (~4 eV) along with spreading. This feature is in good correspondence with theoretical calculation for the ideal DO3 structure. Further increase of the synthesis temperature does not influence on the peak position. However, it activates subsequent peak broadening with strong increase of ELF value in UV region.

3.2.4 Optical conductivity

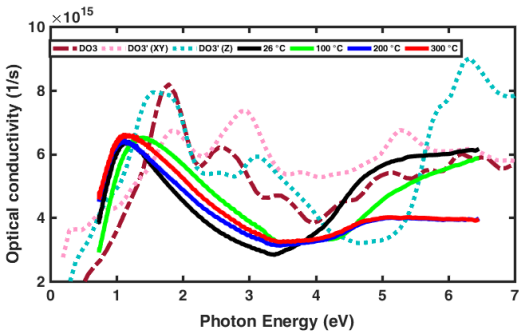

Fig. 6. Optical conductivity of Fe_3Si thin films obtained at different temperatures of Si substrate (solid lines) along with ab initio calculation (dashed lines).

Optical conductivity is mainly formed [10] by free-carriers and links the current density to the electric field. Most prominent peak in experimental curves (Fig. 6) located

around 1 eV, which corresponds to high density of electrons (T_{2g} for Fe2 atoms) slightly below Fermi level [9]. Although the carrier densities are low for high energies (5-6.4 eV) and mainly formed by more localised electrons (T_{2g} for Fe1 atoms), the high carrier mobilities of T_{2g} electrons of Fe2 atoms [9] nevertheless guarantee a large contribution of the free carriers. Thus, this energy region is most sensitive to chemical ordering as it follows from comparison with theoretical curves (Fig. 6).

3.2.5 Absorption coefficient

Absorption coefficient characterises the value of penetration of electromagnetic wave in material and is formed by the excitations due to the interaction of photons and electrons, interband and intraband transitions. Low values of α can cause some inaccuracy in description of the ~30 nm thick Fe_3Si film optical properties with semi-infinite medium model. The low photon energy peak positions (~1 eV) in σ, k and Im(ε) parameters are expected to be the most sensitive to this discrepancy. Thus, this issue requires further detailed examination.

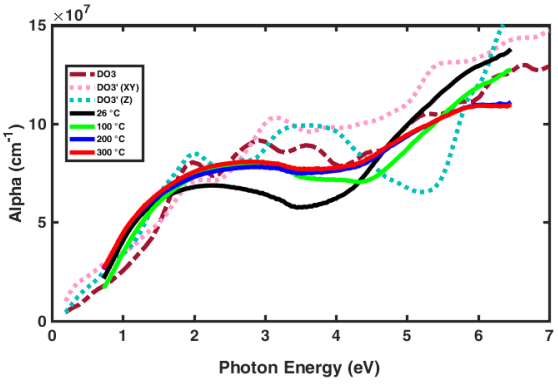

Fig. 7. Absorption coefficient of Fe_3Si thin films obtained at different temperatures of Si substrate (solid lines) along with ab initio calculation (dashed lines).

In general, consideration of α parameter for detection of changes in chemical order is not informative as optical conductivity and ELF, although undergo some distinctive alterations between 3.5 and 4.5 eV.

3.2.6 Reflectivity

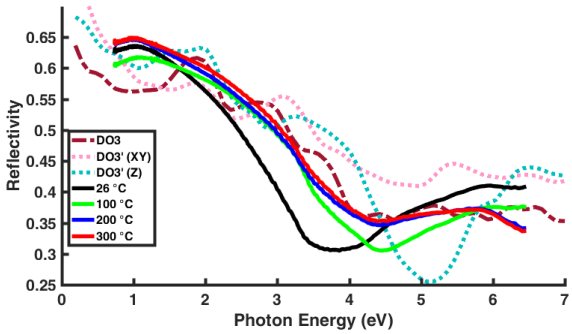

Fig. 8. Reflectivity of Fe_3Si thin films obtained at different temperatures of Si substrate (solid lines) along with ab initio calculation (dashed lines).

Another important optical parameter is reflectivity, which can be measured directly without utilisation of polarimetric techniques. Thus, effect of chemical ordering on reflectivity is found to be essential. Figure 8 reveals that the most sensitive region to chemical ordering lies in higher photon energies (3.2 – 6.4 eV).

4 Conclusions

This work is intended to develop an approach, which would allow us to carry out simple optimisation of growth and annealing conditions of Fe_3Si thin films, by spectroscopic techniques in situ. A simple consideration of the effect of the chemical ordering in Fe_3Si compound on optical parameters by theoretical and experimental methods reveal that electron energy-loss function, optical conductivity and extinction coefficient are sensitive to this phenomenon in different photon energy regions and thus make the whole range (0.74–6.46 eV) useful for the estimation. It is clear, that more deep insight to the problem with consideration of different optical models and various chemical ordering along with involvement of magnetic properties investigation is required and will be discussed soon.

5 Acknowledgements

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