Low temperature formation of β -FeSi₂ polycrystalline microstructure by pulsed laser deposition and thermal annealing

Hiroharu Sugawara,^{1a)} Shingo Nakamura,¹ Masayuki Oouchi,¹
Yui Kumura,¹ Takenobu Shishido,¹ Takatoshi Igarashi,²
Masato Kishi,² and Masahiro Tsuchiya^{2,3}

¹ Department of Electronic Systems Engineering, Tokyo Metropolitan Institute of Technology, 6–6 Asahigaoka, Hino, Tokyo 191–0065, Japan

² Department of Electronic Engineering, School of Engineering,
The University of Tokyo, 7–3–1 Hongo, Bunkyo-ku, Tokyo 113–8656, Japan

³ National Institute of Information and Communications Technology,
4–2–1 Nukui-kitamachi, Koganei, Tokyo 184–8795, Japan

a) hsugawa@cc.tmit.ac.jp

Abstract: β -FeSi₂ polycrystalline microstructure was successfully formed at exceptionally low temperature in the form of droplet with room temperature pulsed laser deposition and post-annealing below 350°C employed. Evidence of the β -phase formation was obtained through microscopic Raman spectroscopy and TEM analysis. The low temperature nature may originate from formation of intermediate amorphous phase possibly provided by quick heat removal from Fe-Si melts generated by laser ablation. This low temperature scheme offers an alternative method of producing polycrystalline β -FeSi₂ without higher temperature processes, which could be beneficially compatible with the standard Si device fabrication processes.

Keywords: β -FeSi₂, group four photonic material, pulsed laser deposition, Raman spectroscopy, low temperature annealing, transmission electron microscopy

Classification: New functional devices and materials

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1 Introduction

Due to its high compatibility with silicon substrates, semiconducting iron disilicide (β -FeSi₂) is one of the materials most suitable for use in silicon-based optoelectronic and photonic integrated circuits. Prior research has proven the production of luminescent β -FeSi₂ participates using methods such as ion beam synthesis (IBS) [1], and molecular beam epitaxy (MBE) growth on FeSi₂ precursors [2]. However, these processes requires successive annealing treatments at 600°C or higher after deposition. Those high temperature processes would cause problems in applying the above methods to conventional silicon fabrication processes and, therefore, should be avoided if possible.

In this study, we report on exceptionally low temperature formation of β -FeSi₂. We found that room temperature pulsed laser deposition (PLD) and thermal annealing at temperatures below 400°C can produce β -FeSi₂ polycrystalline, although it is in a droplet form [3]. We also describe detailed investigation on chemical bonding at the surface of, and the inner microstructure of the polycrystalline β -FeSi₂. They were confirmed through microscopic Raman spectroscopy (MRS) and cross-sectional transmission electron microscopy (TEM) analysis, respectively.

2 PLD and thermal annealing

PLD was performed in a chamber evacuated to a base pressure of 10⁻⁶ Torr. An intense light beam generated by an ArF excimer laser with an emission wavelength of 193 nm was introduced into the chamber and focused to a spot size of roughly 1 mm² on a hot-pressed alloy target with the composition of Fe : Si = 1 : 2. The laser pulse energy density was 10 J/cm² and the repetition

rate was set to be 20 Hz. Si CZ (100) substrates were placed in front of the target at a distance of 40–48 mm. No apparatus such as mechanical filters [4] were used to prevent particles attacking the substrate. The deposition was performed at room temperature for 20 minutes.

For comparison, two kinds of annealing sequences were applied to a set of simultaneously deposited samples. The temperature of Sample #1 was raised stepwise to $T_a = 300, 350$, and 400°C . Each of those three temperatures was maintained for 20 minutes before subsequent cooling to the room temperature. In contrast, Sample #2 was annealed at $T_a = 600^\circ\text{C}$ for 2 hours. The annealing processes were carried out in a N_2 atmosphere in a furnace equipped with an optical window for in-situ MRS measurements.

3 Formation of $\beta\text{-FeSi}_2$ droplets

The inset of Fig. 1 shows an SEM photograph taken for a droplet on Sample #2. PLD generates a large number of such hemispheres, whose diameter and height are both in $10\ \mu\text{m}$ or less, almost irrespective of deposition parameters. So far, such droplets were considered immaterial, and had not been subjected to research [5]. However, we focused our attention on their optical and crystallographic nature.

Fig. 1. Raman spectra measured at room temperature. Curve (a) for the as-deposited condition, curves (b)-(d) for Sample #1 of respective annealing temperatures, T_a , and curve (e) for Sample #2. Inset: SEM photograph of Sample #2.

MRS was carried out at room temperature with a 514.5 nm Ar laser excitation source. The laser beam was focused into a 1 μm diameter spot on the droplet. The scattered light was analyzed by using a grating monochromator which employed a CCD array detector.

Raman spectra (b)–(d) in Fig. 1 correspond to the respective annealing steps of Sample #1. In the case of $T_a = 350^\circ\text{C}$, the Raman peaks at wavenumber shifts of 194 and 248 cm^{-1} were detected, which suggests the formation of $\beta\text{-FeSi}_2$ in the vicinity of the droplet surface. With the rise in annealing temperature, the spectral intensity is enhanced, leading to Raman peaks for Sample #2, which are rather clearer at three particular wavenumbers: 177, 194, and 248 cm^{-1} . Those numbers are in good agreement with those in the literature [6], thus suggesting the formation of $\beta\text{-FeSi}_2$ at annealing temperatures higher than 350°C .

Because MRS only gives of the surface, we then conducted crosssectional TEM analysis of a droplet sliced by focused Ga ion beam. This method provides a positional accuracy of 100 nm.

Fig. 2 shows a TEM photograph for Sample #2. The polycrystalline features are apparent from the presence of domain boundaries. Lattice images and corresponding diffraction patterns obtained therein provide clear evidence of the formation of $\beta\text{-FeSi}_2$.

Fig. 2. Crosssectional TEM photograph of a droplet for Sample #2.

Note that the interface between the substrate and the droplet is quite flat, which suggests the collision of the two does not result in structural damage of the substrate and that the droplet is in liquid-phase before the collision. No epitaxial relationship exists between the droplet and the substrate, implying that $\beta\text{-FeSi}_2$ droplets produced by this method are independent of the substrate lattice. Indeed, we have succeeded in making $\beta\text{-FeSi}_2$ droplets on a glass plate in a similar way with 350°C annealing, which will be reported elsewhere.

In contrast, a TEM image of an as-deposited droplet exhibits neither multiple domain features nor a lattice image. A halo ring is observed in its diffraction image, indicating presence of an amorphous substance and, therefore, supporting the above-mentioned collision model with a liquid-to-amorphous phase transition. It is also noted in the SEM photograph that the

surface of the as-deposited droplets is much smoother than the surface of the annealed droplet. These differences suggest that the annealing process causes the other transition from the amorphous phase to polycrystalline phase.

The annealing conditions, *i.e.*, temperature and duration, necessary for the processes described here are exceptionally mild in comparison with the conventional solid state reaction of Fe with Si which requires both a temperature higher than 450°C, and that that temperature be maintained for a longer time [7]. We speculated about the reasons for this by summarizing the above-mentioned models as follows. First, fused Fe-Si is generated by the laser ablation, and then collides with the substrate surface. Its thermal energy is quite efficiently removed by the Si substrate because of its small volume and the high thermal conductivity of Si. The rapid cooling and resultant supercooling which then occurs could lead to the formation of an amorphous phase. The presence of intermediate amorphous phase could highly assist in the transformation into the β -phase caused by the subsequent low temperature annealing.

4 Summary

On the basis of Raman spectroscopy and TEM analysis we have found that β -FeSi₂ can be formed by an exceptionally low temperature process sequence, using room temperature PLD and thermal annealing below 400°C. The scheme presented here would offer an alternative way to produce polycrystalline β -FeSi₂ without higher temperature processes, which could be beneficially combined into the standard Si device fabrication processes.

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