Epitaxially growth of $\beta$-FeSi$_2$ thin films on Si(100) substrates from $\varepsilon$-FeSi targets with ArF excimer laser deposition

M Tode$^1$, Y Takigawa$^1$, M Ohmukai$^2$, K.Kurosawa$^3$ and M Muroya$^1$

$^1$Osaka Electro-Communication University, Osaka, 572-8530 Japan
$^2$AKASHI National College of Technology, Hyogo, 647-8501 Japan
$^3$University of Miyazaki, Miyazaki, 889-2192 Japan

E-mail:takigawa@isc.osakac.ac.jp

Abstract. We prepare high quality thin films of $\beta$-FeSi$_2$ on silicon substrates by an ArF excimer laser deposition method (ArF-PLD) using $\varepsilon$-FeSi alloy targets. Preferentially [100]-oriented $\beta$-FeSi$_2$ films were grown on Si(100) surfaces, and the interface between the films and substrates are very smooth. Based on a fact that when iron silicide films are obtained on sapphire substrates in stead of the silicon ones, the films have the same compositions as the target materials, silicon atoms in the $\beta$-FeSi$_2$ films must be supplied from the silicon substrates.

1. Introduction

The development of ecologically friendly metal-silicide semiconductor devices is important in order to prevent environmental and ecological degradation and destruction. Iron disilicide, $\beta$-FeSi$_2$, has favorable features and excellent properties in this regard, such as the abundance of its constituents in natural resources and its non-toxicity. $\beta$-FeSi$_2$ has been attracted much attention since luminescence has been reported to have the peak at a wavelength well matched to the transmission windows of optical silica fibers at 1.55 $\mu$m [1-2]. In order to fabricate $\beta$-FeSi$_2$ as the activation material for a light emitting diode (LED) or a laser diode (LD), high quality epitaxially grown (100)-oriented $\beta$-FeSi$_2$ thin films on Si single crystal substrates have been investigated using various thin film growth methods including solid phase epitaxy (SPE)[3], molecular beam epitaxy (MBE)[4] and ion beam synthesis[5]. $\beta$-FeSi$_2$(100) thin films are possible to grow epitaxially on (100) silicon substrates by considering a fact that lattice mismatch between the films and the substrates is less than 5%.

However, these films are including high defect densities and small domain sizes. It has been reported that $\beta$-FeSi$_2$ films are also deposited by a laser deposition method [6-7], but they all are polycrystalline. In order to overcome these difficulties, more work in optimizing the growth process or the use of other deposition techniques will be needed.

Pulsed laser deposition (PLD) is such a promising deposition method that deposition conditions are easily controlled. In this paper, we change the deposition conditions like materials and temperatures of targets and substrates to obtain preferentially [100]-oriented $\beta$-FeSi$_2$ thin films on Si(100) substrates with ArF excimer laser deposition.
2. Experimental

$\beta$-FeSi$_2$ films were grown on Si(100) surfaces by using an ArF excimer laser deposition system in a ultrahigh vacuum growth chamber with a base pressure of $5 \times 10^{-9}$ Torr. The deposition apparatus used in the experiment is shown in Figure 1. Two different materials are used as the targets: $\beta$-FeSi$_2$ ceramic and $\varepsilon$-FeSi alloy ingot. The former one is commercially available. The last one is prepared by ourselves as follows: high purity Fe powders (99.999%) and Si powders (99.999%) are mixed in mol ratio of Fe:Si=1:1.03. The mixture is melted in an argon arc-discharge furnace in argon atmosphere of 1.1 atm to get the alloy, and then the alloy is re-melted in argon gas atmosphere of 20 atm in high pressure furnace that equip with the temperature control circuit. By the 2-step melting method, high quality $\varepsilon$-FeSi alloy ingot with no-pores and no-cracks inside it are obtained. The targets are cut by diamond cutter and the surfaces are polished by diamond powder paste with 1 $\mu$m diameter. Si(100) wafers used as substrates are dipped in dilute HF solution (Hf:H$_2$O=1:20) for 5 min in order to remove the native silicon oxide and the surfaces are passivated by hydrogen termination. The wafers are then rinsed in de-ionized water and mounted onto an Al$_2$O$_3$ ceramic substrate holder in which a Pt heater is equipped with. The substrate is positioned at 4 cm from the target. The experimental apparatus for PLD is shown in Figure 1.

The temperature of the targets is set at room temperature or 973K, while the substrate is kept at 1023K. The laser fluence on the target is roughly 4 J/cm$^2$. The composition and crystal structures of the films are characterized by electron-probe microanalysis (EPMA) and X-ray diffraction patterns (XRD) using CuK$_{\alpha}$ radiation. The surface and cross section morphologies are observed with a secondary electron microscope (SEM).

3. Results and discussion

We will show first crystal structures of films deposited by using the two different targets, $\beta$-FeSi$_2$ ceramics and $\varepsilon$-FeSi ingot. Figure 2 shows the XRD patterns of iron silicide films deposited on the (100) silicon substrate kept at 1023K from the ceramics target. Pattern A is that from a film deposited from the ceramics target kept at room temperature and pattern B is from the ceramics target heated at 973K. Almost all of the diffraction peaks in both patterns are assigned as those of $\beta$-FeSi$_2$ except for some sharps peaks from the silicon substrate. The thin films deposited from the ceramics target are concluded to be $\beta$-FeSi$_2$. Figure 3 shows diffraction patterns of films deposited on Si(100) kept at 1023K from the $\beta$-FeSi target kept at room temperature (C), and heated at 973K (D). These films show also $\beta$-FeSi$_2$ phase.

$\beta$(400), $\beta$(600) and $\beta$(800) peaks are recognized in the figures except for pattern B. These have never been observed in an XRD pattern from $\beta$-FeSi$_2$ powders [8], which shows the strongest peak of $\beta$(202)(220). We conclude, thus, that these peaks come from preferred [100]-orientation of $\beta$-FeSi$_2$. 

![Figure 1. The top view of the experimental arrangement used for pulsed laser deposition.](image-url)
film deposited on (100) silicon substrate. But any preferred orientation was not observed from the film B.

We will use the peak height ratio of $\beta(800)/\beta(202)(220)$ as the degree of [100] preferred orientational growth of $\beta$-FeSi$_2$ in the discussion. Of course bigger ratios indicate higher quality of $\beta$-FeSi$_2[100]$ epitaxy. The ratio of pattern A is 7, B is 0, C is 3.8, and D is 19. We can say, here, that the best quality $\beta$-FeSi$_2[100]$ epitaxial films are deposited on Si(100) substrates from $\varepsilon$-FeSi ingot target kept at 973K(D).

We observe droplets seen on the deposited film surfaces with a SEM. As shown later, the droplets are confirmed to be $\beta$-FeSi$_2$. The densities and sizes are $\sim$300/cm$^2$ and $\sim$3 $\mu$m from the $\varepsilon$-FeSi targets heated at 973K, whereas $\sim$10$^4$/cm$^2$ and $\sim$15 $\mu$m are from both targets kept at room temperature.

We can conclude that material and temperature are the most important factors for preparing the highest quality crystalline $\beta$-FeSi$_2[100]$ films on Si(100) substrates in pulse laser deposition. The best factor in the experiment is in use the $\varepsilon$-FeSi target heated at 973K.

![Figure 2. XRD spectra $\beta$-FeSi$_2$ films by depositing $\beta$-FeSi$_2$ ceramics target on Si(100) substrate at room temperature (A) and 973 K (B).](image)

![Figure 3. XRD spectra $\beta$-FeSi$_2$ films by depositing $\varepsilon$-FeSi target on Si(100) substrate at room temperature (C) and 973 K (D).](image)

Figures 4 and 5 show SEM photographs of cross sections including both of deposited films and substrates. The upper white thin layers are deposited films and the lower dark areas are Si substrates. Photos E and F in Figure 4 show films deposited from room temperature and 973K $\beta$-FeSi$_2$ targets, respectively. In E, the part which swells out on the deposited layer is a droplet. The composition of the droplet is confirmed to be Fe:Si=1:2 by EPMA. The $\beta$-FeSi$_2$ thin layer lies under the droplet. The layer does not adhere to the Si(100) substrate completely and gaps exist in the interface region between the film and substrate. The existence of such gaps means that ablation species from the target cannot grow epitaxially on Si(100) substrate. On the contrary, in F such gaps are not observed but the interface is not smooth and the film is not flat. Photos G and H in Figure 5 show films deposited from room temperature and 973K $\varepsilon$-FeSi targets, respectively. In the cases of using $\varepsilon$-FeSi targets, the common feature is no gaps and different feature is interface. The interface line is smoother in photo H than that in G. The thickness of the films in H is about 150nm. We can say, here, that smooth and good interfaces are obtained from $\varepsilon$-FeSi targets heated at 973K.

Now, we have a question about the composition difference between the $\beta$-FeSi$_2$ films and $\varepsilon$-FeSi targets, namely where silicon atoms in $\beta$-FeSi$_2$ films come from. There may be two possibilities, (1) even though equal numbers of Fe and Si ions are ejected from the targets, $\beta$-FeSi$_2$ is more stable than
\( \varepsilon \)-FeSi at 1023 K, and (2) silicon atoms are supplied from silicon substrates. When sapphire substrates are used instead of silicon substrates, the film composition is the same as the target, namely iron silicide films are deposited on sapphire substrates from \( \varepsilon \)-FeSi targets. By considering the result, silicon atoms in the \( \beta \)-FeSi\(_2\) films are supplied from the silicon substrates. Such silicon atom diffusion between the targets and films must promote the high quality epitaxy.

**Figure 4.** SEM pictures of cross section of \( \beta \)-FeSi\(_2\) films deposited from \( \beta \)-FeSi\(_2\) ceramics target on Si(100) substrates at room temperature (E) and 973 K (F). The film thickness is about 200 nm in F.

**Figure 5.** SEM pictures of cross section of \( \beta \)-FeSi\(_2\) films deposited from \( \varepsilon \)-FeSi target on Si(100) substrates at room temperature (G) and 973 K (H). The film thickness is about 150 nm in H.

### 4. Conclusions
Iron silicide films are deposited on Si(100) substrates kept at 1023 K from \( \varepsilon \)-FeSi alloy targets and \( \beta \)-FeSi\(_2\) ceramic targets at room temperature or heated at 973 K by ArF-PLD. The highly oriented epitaxially \( \beta \)-FeSi\(_2\)(100) films on Si(100) substrates without any fragments were deposited, and the interfaces between the \( \beta \)-FeSi\(_2\) films and Si(100) substrates were smooth. In order to grow the \( \beta \)-FeSi\(_2\)(100) film on the Si(100) substrate, ablated Fe and Si ions ejected from \( \varepsilon \)-FeSi targets react with silicon atoms of Si substrates. The growth technique to make smooth interfaces of \( \beta \)-FeSi\(_2\) thin films and silicon substrates by ArF-PLD will apply to fabricate junctions required for \( \beta \)-FeSi\(_2\) thin film light emitting devices.

### References
[1] M.C.Bost and J.E.Mahan 1985 J.Appl.Phys. 58 2696
[2] D.Leong, M.Harry, K.J.Reeson and K.P.Homewood 1997 Nature 387 686
[3] H.Chen, P.Han, X.D.Huang and Y.D.Zheng 1996 J.Vac.Sci.Techmol.A 14 905
[4] T.SUNOHARA, C. LI, Y.OZAWA, T.SUEMASU and F.HASEGAWA 2005 Jpn.J.Appl.phys. 44 3951
[5] Y.MAEDA, Y.TERAII and M.ITAKURA 2005 Jpn.J.Appl.phys. 44 2502
[6] Z.Liu, M.Okoshi and M.Hanabusuma 1999 J.Vac.Sci.Techmol.A 17 619
[7] T.Yoshitake, T.Nagamot and K.Nagayama 2001 Thin Solid Films 381 236