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STRUCTURAL AND OPTICAL PROPERTIES OF SPUTTER DEPOSITED $FeSi_2$ THIN FILMS

M. Milosavljević[1,2], L. Wong[2], M.A. Lourenço[2], R. Valizadeh[3], J.S. Colligon[3], G. Shao[4], and K.P. Homewood[2]

[1]VINČA Institute of Nuclear Sciences, POB 522, 11001 Belgrade, Serbia
[2]Faculty of Engineering and Physical Sciences, University of Surrey, Guildford GU2 7XH, UK
[3]Department of Chemistry and Materials, Manchester Metropolitan University, Manchester, M1 5GD, UK
[4]Centre for Materials, Research & Innovation, University of Bolton, Bolton BL3 5AB, UK

ABSTRACT

This paper reports on the synthesis, structural and optical analysis of sputter deposited amorphous and polycrystalline $FeSi_2$ thin films. A range of deposition temperatures, from room temperature (RT) up to 700°C and post-anneals between 300 and 700°C were performed. For deposition temperatures from RT to 300°C the grown films had an amorphous structure, while those deposited at 400-700°C had a crystalline β-$FeSi_2$ structure. Heat-treated films remained amorphous up to 400°C, and at 500°C and higher temperatures they transformed to crystalline β-$FeSi_2$. Optical absorption measurements showed that the band gap is direct in nature ranging from 0.897 to 0.949 eV. The deposition temperature was seen to affect the crystallinity of the as-deposited thin films and to vary both the optical and structural properties of the layers significantly. For amorphous thin films the band gap value and absorption coefficient increased significantly upon annealing above 500°C. This was found to be in good agreement with the transformation of the silicide from its amorphous phase to its crystalline β-phase.

Index Terms – Silicides, iron-disilicide, photo-absorption, amorphous semiconductor, TEM

1. INTRODUCTION

Semiconducting transition metal-silicides have attracted a significant attention for many years due to their potential applications in optoelectronics and microelectronics [1]. Iron-disilicide is an interesting optoelectronic material, being a narrow band gap direct semiconductor (E_g=0.85–0.95 eV) both in its crystalline β-phase [2] and in amorphous phase [3], as well as in the form of very fine (3–5 nm) β-$FeSi_2$ nano-crystals [4]. Such properties allowed successful fabrication of a silicon-based light-emitting device, consisting of β-$FeSi_2$ precipitates embedded in a Si matrix [5]. Furthermore, iron-disilicide has a high photo-absorption coefficient, good thermal stability, corrosion resistance, and consists of non-toxic materials, which make it a promising material for potential applications in large area electronics and for fabrication of solar cells [6-9].

In this paper we report on the synthesis and optical transmission measurements of $FeSi_2$ films to study the annealing and deposition temperature influence on optical properties such as the band gap and absorption coefficient, in conjunction with structural analysis. The films were deposited on Si (100) wafers by ion sputtering, at substrate temperatures ranging from room temperature (RT) to 700°C. The as-deposited amorphous films were additionally heat-treated at 300-700°C to study the effects of post-deposition processing on their structural and optical properties.

2. EXPERIMENTAL PROCEDURES

The $FeSi_2$ films were deposited by co-sputtering of Fe and Si from a target composed of these two elements. The deposition chamber is equipped with two low energy Ar ion guns, one of which is used for sputtering of the target material and the other for ion beam assisted deposition (IBAD), as described elsewhere [10]. The base pressure in the chamber was in the 10^{-7} mbar range, and the $FeSi_2$ films were deposited to a total thickness of 300–400 nm. The substrates used were Si (100) wafers, held at temperatures ranging from RT to 700°C during deposition. Samples deposited at RT, which were found to be amorphous, were additionally heat-treated, for 30 min at 300-700°C in a rapid thermal annealer.

Stoichiometry of the layers and uniformity of Fe and Si depth profiles were analyzed by Rutherford backscattering spectroscopy (RBS), using a 1.5 MeV He^+ ion beam. Structural analysis was done by transmission electron microscopy (TEM), using Philips EM 400 T and CM 200 microscopes, operated at 120 and 200 keV, respectively. The samples were prepared for cross-sectional analysis. Selected area diffraction and micro-diffraction (MD) analyses were used to identify the phases. Energy dispersive x-ray

spectroscopy (EDX) with a nanobeam probe was also carried out, to verify the layer composition and uniformity. Optical absorption measurements were carried out in transmission, using a tungsten lamp and a quarter meter spectrometer to monitor the transmitted light, as described elsewhere [11].

3. RESULTS AND DISCUSSION

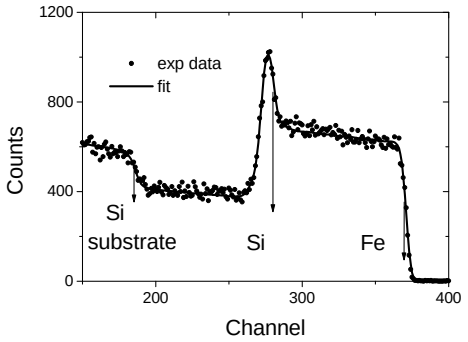

Figure 1 RBS analysis of $FeSi_2$ film as-deposited at RT, showing a random experimental spectrum near [100] Si and the simulation fit.

Analysis of the layer stoichiometry by RBS and EDX has shown uniform Fe and Si depth profiles in all as-deposited and annealed samples, with a concentration ratio within 1-2 at% of the $FeSi_2$ stoichiometry [12]. An example is given in Figure 1, showing a random near-normal incidence RBS spectrum taken from a sample as-deposited at RT. Simulation of the spectrum gave the exact $FeSi_2$ stoichiometry. Taking the bulk density of β-$FeSi_2$ (7.95×10^{22} at/cm^3), the calculated layer thickness of 310 nm matched the value measured by TEM.

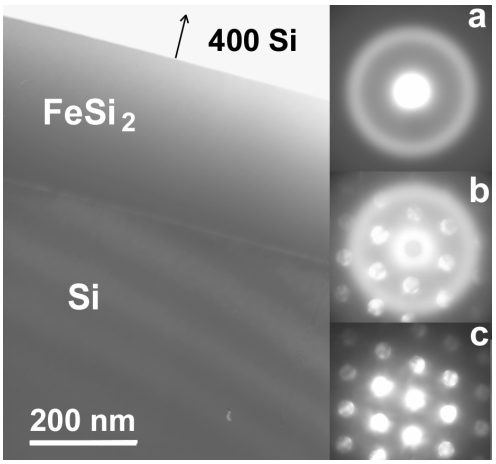

Figure 2 Cross-sectional TEM image of the $FeSi_2$ layer deposited at 200°C, with MD patterns from the layer (a), the layer/substrate interface (b) and the Si-substrate at [011] (c).

The results of TEM analysis have revealed that the $FeSi_2$ films as-deposited at RT, 100 and 200°C have an amorphous structure. The same is for samples as-deposited at RT and subsequently annealed at 300 and 400°C. A typical analysis that demonstrates this structure is given in Figure 2. It shows a bright field cross-sectional TEM image taken from an as-deposited film at 200°C. The image was taken near the [110] Si zone axis. The Fe-silicide layer exhibits a featureless image, where no contrast changes could be observed by sample tilting. The corresponding MD pattern (a) from this region indicates a fully amorphous structure. MD pattern taken from the interface (b) shows diffuse ring pattern from the amorphous layer superimposed on the [011] Si pattern from the substrate, and (c) shows diffraction from the Si substrate in the [011] zone axis.

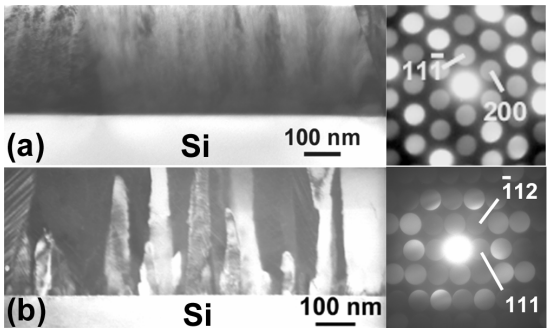

Figure 3 Bright field TEM image (a) of an as-deposited film at 300°C, and dark field TEM image (b) of an as-deposited film at 500°C. The corresponding MD patterns were taken from a single β-$FeSi_2$ grain in each case.

For substrate temperatures ranging from 300-700°C the as-deposited films grow in the form of a polycrystalline β-$FeSi_2$ phase. Figure 3 presents a bright field XTEM image of a layer deposited at 300°C and a dark field image of a layer deposited at 500°C. It is seen that the layers grow in a columnar structure, with individual crystal grains stretching from the Si substrate to the surface. Lateral dimensions of the grains increase from 30-50 nm for the deposition temperature of 300°C up to above 100 nm for the higher deposition temperature. A detailed electron diffraction analysis has identified these grains as β-$FeSi_2$ crystals. The MD patterns presented in the figure were taken from a single grain in each case. The [011] β-$FeSi_2$ orientation in (a) was found close to [110] Si zone axis, where we also found $[1\,\bar{1}\,2]$ oriented β grains. For the higher deposition temperature the β grains are oriented slightly off the main Si zone axis, the $[1\,\bar{3}\,2]$ β-$FeSi_2$ shown in (b) being ~3° off [110] Si.

Figure 4 presents cross-sectional TEM analysis of initially amorphous $FeSi_2$ layers after their annealing

at 500 and 600°C. The identified phase is β-$FeSi_2$, but the layer structure is markedly different compared to the layers as-deposited at these temperatures. As seen from the bright field image taken from the sample annealed at 500°C, the layers crystallize in form of relatively large grains of up to a few hundred nm with a random orientation, practically not influenced by the Si substrate. The enclosed MD pattern shows a [001] orientation of a β-$FeSi_2$ grain, which was found far away from any low-index Si planes. These relatively large grains have irregularly shaped grain boundaries, some of them containing β-$FeSi_2$ nanocrystals. Some of the large grains also contain β-$FeSi_2$ nanocrystals, as seen in the dark field image taken from a sample annealed at 600°C. Nanocrystals appear as bright features in the image and give a sharp diffraction ring in the MD pattern taken from this area. The pattern was taken off a main crystal zone axis, as the contrast of the ring is rather weak. The position of the ring coincides with the strong (400) reflection from a larger β-$FeSi_2$ grain.

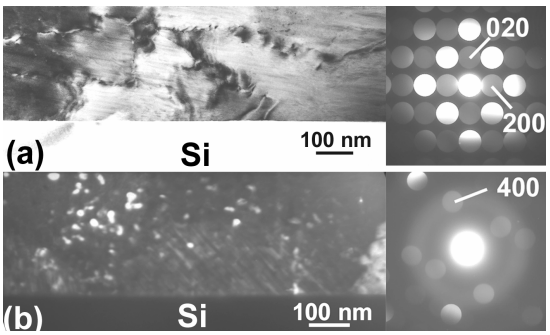

Figure 4 TEM analysis of initially amorphous films: bright field image (a) of a sample annealed at 500°C, and dark field image (b) of a sample annealed at 600°C. MD patterns identify a β-$FeSi_2$ grain (a) and a diffraction ring originating from β-$FeSi_2$ nanocrystals (b).

The effect of increasing the substrate temperature to 700°C is illustrated in Figure 5, showing bright field cross-sectional TEM images of an as-deposited and an annealed sample, both taken near [110] Si. The as-deposited layer grows in form of much larger β-$FeSi_2$ grains compared to the lower deposition temperatures, resulting in a pronounced surface topography. The growth is still strongly influenced by the substrate, though the grains are more relaxed and oriented 4-5° off [110] Si. The annealed layer crystallizes also in form of large β-$FeSi_2$ grains, but again their crystallographic orientation is not influenced by the substrate. The surface of the layer remains smooth, though larger grains still contain nanocrystals of the same phase. A partial lift off from the substrate can be seen at the grain boundary, suggesting that internal stress builds up in the layer during crystallization.

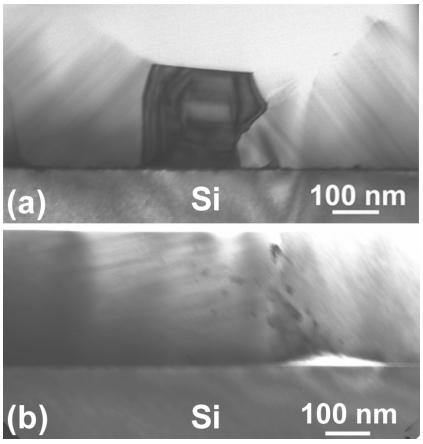

Figure 5 Bright field TEM images from: (a) as-deposited film at 700°C, and (b) initially amorphous film annealed at 700°C

The results of TEM analysis imply that the growth and crystallization in as-deposited $FeSi_2$ layers is controlled by surface diffusion [12]. For the substrate temperature from RT to 200°C, the adsorbed atomic species have insufficient mobility for crystallization. At 300°C and higher temperatures their mobility enables their diffusion at the substrate surface and formation of a crystalline structure. Columnar structure suggests a layer by layer growth. Higher temperatures yield larger and more relaxed β-$FeSi_2$ grains. In the films deposited at 700°C the adsorbed atoms have a sufficient mobility to follow the structure of large under-laying grains, resulting in a developed surface morphology. In case of the films that were as-deposited in an amorphous form, crystallization upon annealing is controlled by bulk diffusion [12]. For this reason the $FeSi_2$ films retain an amorphous structure after annealing for 30 min at 400°C, while at 500°C they fully transform to crystalline β-$FeSi_2$ phase. Having the $FeSi_2$ stoichiometry, the atomic species don't need to diffuse long distances, resulting in a structure different from that of the as-deposited crystalline layers. Crystallization from an amorphous $FeSi_2$ phase proceeds randomly and practically with no influence from the Si substrate. In this random process nano crystals of the same phase nucleate independently and remain incorporated in larger grains or at grain boundaries. Their presence is reduced with increasing the annealing temperature, but also a tensile stress builds up in the layers due to a different expansion coefficient compared to the Si substrate.

Optical absorption measurements on both as-deposited and annealed samples were carried out at room temperature [13]. In Figure 6 we have plotted the square of absorption coefficient versus photon energy. A linear dependence was observed for all α^2

spectra plots towards the higher photon energy range (above 1 eV). This therefore indicates that all samples, both the as-deposited and annealed up to 700° C, exhibit a direct band gap behavior as is seen with the crystalline phase. A summary of the results of the linear extrapolation is shown in Table 1. A range of band gap values between 0.897 and 0.949 eV were observed. These band gaps are comparable to published results for both amorphous and polycrystalline samples fabricated by IBM [14], ion beam synthesis (IBS) [15] and evaporation techniques such as molecular beam epitaxy (MBE) [16].

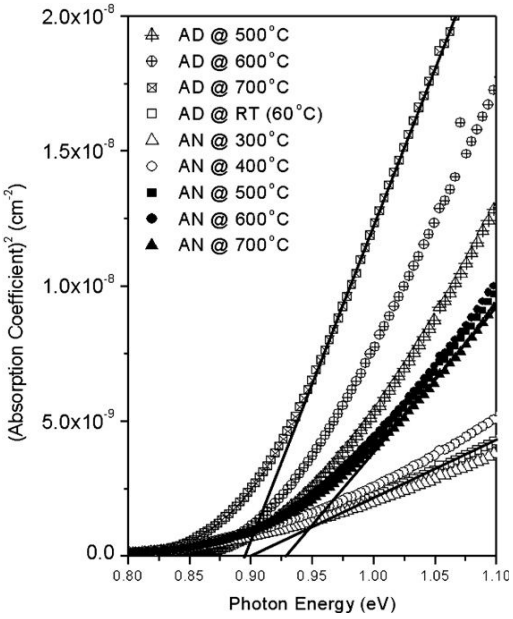

Figure 6 Absorption coefficient squared as a function of photon energy for the as-deposited and annealed samples, where AD and AN stand for as-deposited and annealed, respectively. Shown on the plot are the least-squares linear extrapolation to $\alpha^2 = 0$, for samples AN700, ADRT and AD700.

It can be seen that sample ADRT, which was as-deposited at room temperature only, exhibited an absorption coefficient of 5.29×10^4 cm^{-1} at 1 eV just above its band gap. Comparing these results with those of $\sim 10^2$ for Si [17,18], $\square 10^3$ for a-Si:H [17], $\square 10^4$ for GaAs [17,18] and $\square 10^5$ for CdTe [19], we see that we have an unprocessed material which absorbs better at equivalent energies above their band gaps. For sample AD700, we have an absorption coefficient in the same region as highly crystalline CdTe, currently one of the leading materials for thin film solar cells. The samples annealed at 300 and 400°C exhibit very similar fundamental absorption (above their band gap value), as do the samples annealed between 500 and 700°C. This indicates that the annealing temperature has little effect on the optical properties of the layers until a threshold temperature, between 400 and 500°C, was reached. At this point an increase in band gap values from approximately 0.9 to 0.925 eV and an increase in α, for each sample, were seen to approximately double at equivalent photon energies. Again, further annealing showed little further effect on the optical properties.

Table 1. Summary of the optical band gap and absorption of amorphous and polycrystalline $FeSi_2$ films.

Sample	Annealed/As-dep. at temperature (°C)	Band gap (eV)	α at 1.0 eV (cm^{-1})
AN300	Annealed at 300	0.897 (direct)	5.02×10^4
AN400	Annealed at 400	0.898 (direct)	5.66×10^4
AN500	Annealed at 500	0.926 (direct)	7.30×10^4
AN600	Annealed at 600	0.925 (direct)	7.44×10^4
AN700	Annealed at 700	0.929 (direct)	7.07×10^4
ADRT	As-dep. at RT	0.9 (direct)	5.29×10^4
AD500	As-dep. at 500	0.949 (direct)	8.14×10^4
AD600	As-dep. at 600	0.923 (direct)	9.79×10^4
AD700	As-dep. at 700	0.897 (direct)	1.23×10^5

4. CONCLUSIONS

Amorphous and polycrystalline $FeSi_2$ films were sputter deposited on Si (100) wafers. An investigation into the annealing and deposition temperature dependences on the optical properties has been carried out, in relation to the structural changes within the films. It was seen that all samples, including those observed to be of the amorphous phase, exhibited direct band gaps between 0.897 and 0.949 eV. The deposition temperature was seen to exhibit the largest effect on as-deposited microstructures and associated optical properties. An increase in deposition temperature resulted in a structural transition from amorphous to crystalline thin films with improved crystallinity, and hence a reduction in band gap energies and significant increase in absorption coefficient α. On the other hand, for materials with amorphous as-deposited microstructure, only annealing above 500°C was seen to trigger crystallization and increase the band gap and absorption coefficient. Comparison with published absorption coefficients for c-Si, a-Si:H and GaAs shows that even the unprocessed sample (ADRT) with amorphous microstructure exhibited higher absorption at equivalent energies. In conclusion, we have demonstrated that the optical properties of amorphous and polycrystalline $FeSi_2$ fabricated by sputter deposition can be manipulated by changing the deposition temperature or by post-deposition annealing.

5. ACKNOWLEDGMENTS

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