

**Raman and magneto transport studies of MBE grown
 β -FeSi₂, β -(Fe_{1-x}Cr_x)Si₂, and β -(Fe_{1-x}Co_x)Si₂**

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ABSTRACT

Iron disilicide shows great promise as a silicon based light emitter operating in the 1.3 to 1.5 μm wavelength range. However, there exists a number of questions related to the band structure and the ability to alloy and controllably dope the material both n and p type. In this paper we present Raman and magneto transport studies on β -FeSi₂, β -(Fe_{1-x}Cr_x)Si₂, and β -(Fe_{1-x}Co_x)Si₂ grown by MBE. By comparing the spectra obtained for undoped and doped samples we provide a general overview of the effects of doping on the crystallinity of the material. The temperature dependent (4K<T<300K) magneto transport illustrates that Cr is a p-type dopant and Co is an n-type dopant in β -FeSi₂. The temperature dependence of the resistivity indicates that the transport properties at higher temperatures are determined by free carriers whereas at lower temperatures impurity band conduction prevails.

INTRODUCTION

β -FeSi₂ is unique among the transition metal silicides in that it is the only electro-optically active member of this family of materials and has consequently attracted considerable fundamental and technological interest during the past decade [1]. The low cost and nontoxic nature of the constituent materials make the compound especially inviting for use in today's silicon based technologies [2-4]. Measurements of the absorption coefficients have revealed both direct [5-7] and indirect [8,9] band gaps. Furthermore, bulk and relaxed MBE grown thin films

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of β -FeSi₂ do not exhibit significant light emission [1,4]. However, strained β -FeSi₂ has been predicted to exhibit promising photoemission characteristics [10-14]. These properties have been explained in terms of a quasi-direct band gap [15-17] in unstrained β -FeSi₂, which may be converted to a direct band gap with strain modification.

An alternative to strain is band structure modification due to alloying. Cr and Co are promising elements for both doping and alloying of β -FeSi₂ [1,4]. Cr is a p-type dopant for iron disilicide; the addition of Co yields n-doped films. So far, there is a lack of basic knowledge on the electronic properties of this material. Published data of the room-temperature (RT) mobility of free carriers in thin films scatter broadly in the range 1-100 cm^2/Vs [18-24].

Raman spectroscopy is a very useful tool for obtaining information related to the structure and bonding of semiconducting materials [25-28]. In addition to our Raman results, we report on the temperature dependence of the resistivity, concentration and mobilities of undoped, Cr-doped and Co-doped β -FeSi₂ layers prepared by MBE.

EXPERIMENTAL

Epitaxial β -FeSi₂, β -(Fe_{1-x}Cr_x)Si₂, and β -(Fe_{1-x}Co_x)Si₂ films were grown in an ultrahigh vacuum MBE growth chamber on Si(100) and Si(111) substrates with 1-5 k Ω cm resistivity using the template technique. Further details of this growth technique and sample preparation can be found elsewhere [29].

The samples investigated in this study are listed in Table I. The three types of samples were nominally undoped (p-type), Cr-doped (p-type), Co-doped (n-type). The film thickness values were obtained from photometry, spectroscopy ellipsometry, and Rutherford backscattering (RBS). The amount of dopants in the films (Cr, Co) was determined either by energy dispersive X-ray microanalysis (EDX) or from RBS.

Micro-Raman spectra were obtained with a JY U1000 Raman system. The spectrometer

TABLE I

Sample No.	Substrate	Concentration	Thickness (optical)	Thickness (RBS)	μ (cm^2/Vs) (At 77 K)	μ (cm^2/Vs) (At 300 K)
344	n-Si(100)	-	251nm	250nm	91	199
358	n-Si(100)	X _{Cr} =0.003 (EDX)	-	250 nm	79	84
324	n-Si(111)	X _{Cr} =0.006 (EDX)	268nm	-	23	43
367	p-Si(100)	X _{Co} =0.009 (RBS)	282nm	264nm	3	18
352	p-Si(100)	X _{Co} =0.066 (RBS)	290 nm	266 nm	See text	See text
353	p-Si(100)	X _{Co} =0.14 (RBS)	307 nm	273 nm		

consists of two coupled 1 meter monochromators equipped with a pair of 1800 grooves/mm holographic gratings. The spectra were measured in the backscattering configuration using the 514.5 nm line of an Ar ion laser as the excitation source (resulting in a penetration depth, d_p , of about 18 nm). The output power of the argon laser was maintained at 100 mW, and the light was filtered through a Pellin-Broca prism system and focused onto the sample through an Olympus microscope with a 100X objective. This provided a spot size of about $5\mu\text{m}$. The laser power at the sample was ~ 6 mW, and the scattered light was detected by a Peltier cooled GaAs photomultiplier tube. All spectra were obtained with the samples at room temperature, and the Raman frequency shifts were calibrated against a Hg source. The location of the main A_{1g} Raman peak at 247 cm^{-1} is accurate to within $\pm 0.05\text{ cm}^{-1}$.

For the electrical measurements, the contacts to the samples were made using colloidal silver in a four-point configuration. The Ohmic character of the contacts was checked by coplanar I-V measurements. The temperature dependence of the resistivity, concentration and the mobilities were studied in the range 4-300K. The strength of the magnetic field used was kept constant at 1.9T as measured by a Hall probe mounted near the sample.

RESULTS AND DISCUSSION

Comparing spectra for the undoped film on Si(100) to the one for the Cr-doped sample with $X_{\text{Cr}} = 0.003$ on Si(100) as seen in Figure 1(a), the Raman peak increases slightly in intensity, sharpens, and shifts closer to the peak position for the single crystal. This suggests that the crystalline quality of the silicide improves with Cr doping. In contrast to the previous, spectroscopic ellipsometry measurements of these materials [30]. Our Raman results suggest that Cr helps to stabilize the crystal structure and promote stoichiometric growth. This was found to be the case for $\beta\text{-OsSi}_2$ [31], which happens to be isostructural to $\beta\text{-FeSi}_2$. We realize that these results are very preliminary, and that detailed investigations of the growth mechanism will have to be carried out to confirm this hypothesis.

The Raman spectra of the Cr-doped sample with $X_{\text{Cr}} = 0.006$ on Si(111) reveals a structure only slightly less intense, broader, and red shifted, as compared to the undoped film on Si(100). This indicates that Cr-doped films of high quality can also be grown on Si(111). Figure 1 (b) compares the Raman spectra of the A_{1g} for the undoped film and the Co-doped samples. We find that as the Co concentration increases, the Raman peak is reduced greatly in intensity, broadens, and shifts strongly to the red. These results are consistent with a loss in crystalline quality. However, a red shift of $\sim 10\text{ cm}^{-1}$ is larger than the crystalline quality would predict. Therefore, we suggest that the larger mass of the Co atom also contributes to the red shift. Normally, the phonon spectra in semiconducting silicides are largely influenced by the bonding properties (force constants) and not by the mass of the metallic component [4], however, recent results on $\beta\text{-OsSi}_2$ [32] suggest that the greater mass does indeed lead to a considerable red shift of the phonon spectra.

Figure 2 (a) compares the temperature dependence of the resistivities of undoped, p-type Cr doped and n-type Co doped samples. When the material is doped with small amount of Cr ($X_{\text{Cr}}=0.003$) the resistivity decreases by a factor of 7 (about $5 \times 10^{-2}\Omega\text{cm}$) when compared with the undoped sample. A further increase in the amount of Cr ($X_{\text{Cr}}=0.006$) does not influence this value significantly. The resistivity for Cr doped sample was found to be $9 \times 10^{-2}\Omega\text{cm}$ at 300K.

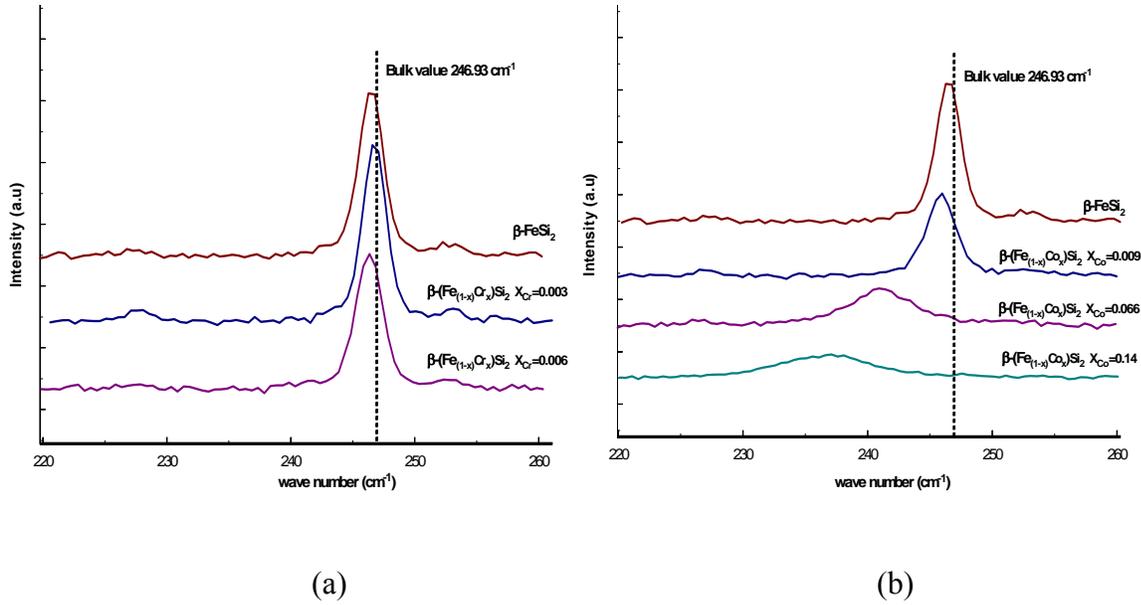


Figure 1: The A_{1g} Raman peak for the (a) Cr doped samples and (b) Co doped samples are shown for comparison. The Raman spectra for the nominally undoped sample is included in both (a) and (b), and the vertical line at 246.93 cm^{-1} represents the peak position for fully relaxed single crystalline $\beta\text{-FeSi}_2$.

Reduction of ρ compared with the undoped sample arises as a result of the change of the dominant transport mechanism from defect band to valence band conduction [24].

When the material is doped with small amount of Co ($X_{\text{Co}}=0.009$) the resistivity decreases by a factor of 3. The resistivity decrease with increasing Co content indicates an increase in the charge carrier concentration.

Lowering the temperature resulted in a strong increase of ρ in all samples. The resistivity data of the Cr doped and the Co doped samples suggest the existence of two temperature regions with a transition region between them. (1) $T > 100\text{K}$: In this region the resistivity decreases, due to the thermal ionization. (2) $T < 50\text{K}$: In this region the resistivity increases with the decreasing temperature, due to the freeze out of the free carriers.

Figure 2 (b) shows the temperature dependence of the carrier concentration for the Cr, Co and the undoped sample. The Co doped sample exhibits n-type conduction, whereas both the Cr doped and undoped samples exhibit p-type conduction. The carrier concentration of the Cr doped sample is greater than the undoped sample at 300K, but decreases to a value that is less than the undoped sample at low temperatures. This indicates that the undoped sample has a larger concentration of unknown p-type impurities.

Table 1 shows the mobilities of all the samples at 300K and 77K. We observe that the mobility of the Cr doped sample is less than the undoped sample and it further decreases with the increase in the Cr content. In addition, the mobility of the Co doped sample is less than that of the undoped sample but as the amount of the Co concentration is increased the mobility increases.

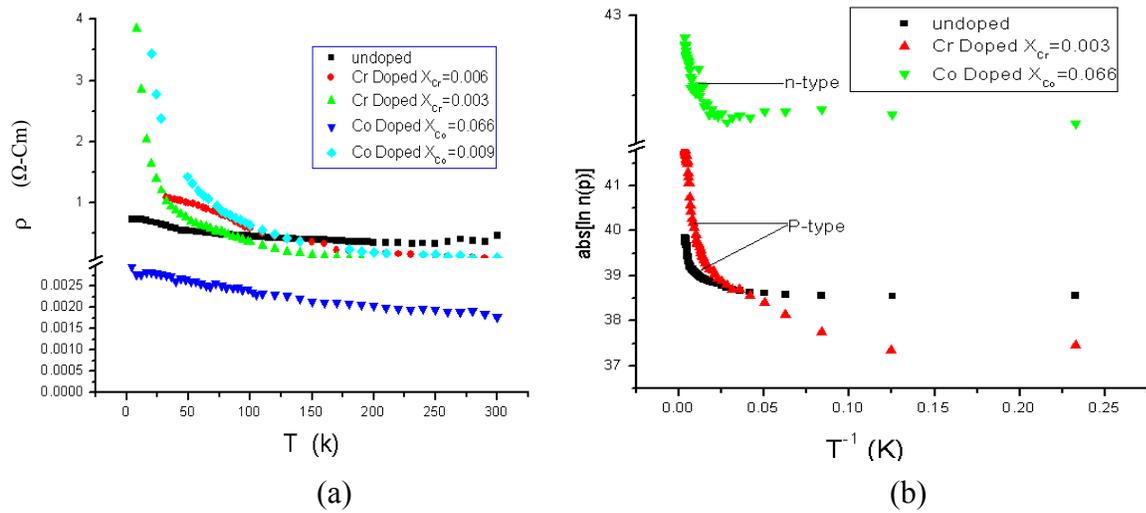


Figure 2: Temperature dependence of (a) resistivity (b) Carrier concentration for undoped, Cr doped and the Co doped samples is shown for comparison.

SUMMARY

Raman spectra of MBE grown $\beta\text{-FeSi}_2$ show an improvement of crystalline quality of the silicide with Cr doping and loss in crystalline quality with Co doping. The Cr doped $\beta\text{-FeSi}_2$ showed good transport properties, which are consistent with the Raman results. The magneto transport studies indicate different conduction mechanisms in Cr and Co doped samples.

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