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Ion beam synthesis of Mg_2Si

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The semiconducting metal silicides and Mg_2Si in particular have been extensively studied in the last few years because of the following reasons: the materials have the potential to be successfully integrated in the optoelectronic silicon technology, the materials are nontoxic and the constituting elements are found in a large amount in nature, and lastly the formation of nanocrystals in a perticular matrix offers the possibility of semiconducting structures with new properties.

The Mg-Si phase diagram [1] shows that Mg_2Si is the only silicide in this system and it melts congruently at 1085 °C. Therefore, crystal growth from the melt should be possible, but one has to be careful about the considerable evaporation of the Mg component as the boiling point of pure Mg is very close to the compound melting temperature. Growth by chemical vapor transport is hardly possible because of the lack of stable magnesium halides and the growth of Mg_2Si bulk material has been accomplished exclusively from a melt [2–5].

The compound Mg_2Si has, similar to Si, a cubic structure with a larger lattice parameter. The lattice mismatch for the Mg_2Si (111) face on the Si (111) face is 1.9%. Due to the comparatively small lattice mismatch high quality epitaxial growth of Mg_2Si onto monocrystalline silicon appears to be possible [6]. However thin film formation is difficult because of the low condensation and high vapor pressure of Mg and that is why thin film preparation and studies are scarce. The first reports on Mg_2Si thin film formation [7, 8] note that the silicidation proceeds rather rapidly in Mg/Si thin film substrates at relatively low temperatures and silicide columns matching the monocrystalline silicon substrate are formed. There has been an attempt to fabricate Mg_2Si by laser melting of magnesium film deposited on a Si substrate [9]. The synthesized layers contain both silicides and Si crystallites. Mahan *et al*. [10] have prepared Mg_2Si films, textured in the (111) direction by molecular-beam epitaxy. They find that intended reactive deposition of magnesium onto silicon substrate at temperatures from 200 to 500 °C results in no accumulation of magnesium. However, codeposition of magnesium and silicon at 200 °C, using a magnesium-rich flux ratio, gives stoichiometric Mg_2Si films. A solid-phase growth technique with preliminary formation of templates was used by Galkin *et al*. [11] to prepare continuous Mg_2Si films with a thickness of the order of 20 nm on Si (111) substrates.

The very low condensation coefficient of magnesium as well as the limited Mg_2Si films thickness due to the barrier behavior of Mg_2Si can be overcome using the ion-beam synthesis (IBS) method, reported in this paper.

The samples were prepared by IBS, followed by rapid thermal annealing (RTA). The implantation of $^{24}Mg^+$ ions was performed using an ion accelerator type ILU-4, allowing a high current density. As an ion plasma source 4N pure Mg, heated at 500 °C, was used. The vapor pressure of Mg at this temperature is about 10^{-2}–10^{-1} Torr. During the implantation, in order to avoid amorphization [12], the substrates were heated to a temperature of about 230 °C by means of the incident ion beam (current density 10–12 $\mu A \cdot cm^{-2}$). The mass separated $^{24}Mg^+$ ions were implantated into *n*-type Si wafers with (100) orientation and resistivity 4.3–4.5 Ω·cm. Four types of samples were prepared. The first two types were fabricated by two-step ion implantation with two different doses—5×10^{16} and 1×10^{17} cm^{-2}, with energies 15 and 40 keV respectively. The other two types of samples were prepared by one-step implantation of two different higher doses—2×10^{17} and 4×0^{17} cm^{-2} with energy 40 keV. The Mg implantation profiles were simulated by SRIM (Stopping and Range of Ions in Matter) and the initial profiles of the implanted Mg ions were estimated as:

$$C(Mg) = \{N(Mg)/[N(Mg) + N(Si)]\} \cdot 100[at.\%],$$

where the N values are the densities of the Mg and Si atoms in cm^{-3}. The concentration of the magnesium ions as a function of the implantation depth for the different types of implantation is shown in Fig. 1. As seen from the figure the Mg concentration is lower than the Mg_2Si stoichiometric one, 66.66 at.% Mg, for all four types of samples. Thus the fabricated Mg_2Si phase is most probably in the form of precipitates—nanocrystals.

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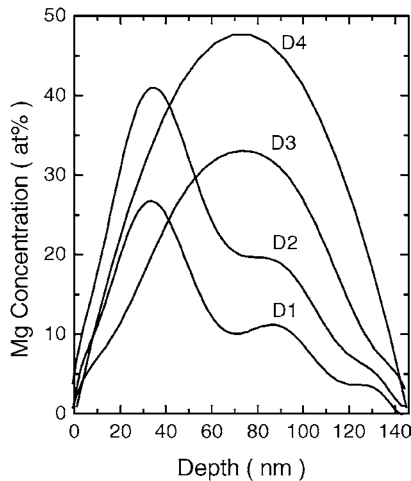

Figure 1 The Mg ions implantation profiles at four different doses: $D_1 = 5 \times 10^{16}$ cm^{-2}, $D_2 = 1 \times 10^{17}$ cm^{-2}, $D_3 = 2 \times 10^{17}$ cm^{-2}, and $D_4 = 4 \times 10^{17}$ cm^{-2}, each of the first two implanted with energies 15 and 40 keV and the remaining two with energy 40 keV.

After the implantation all types of samples were annealed at the same temperature—500 °C, which is lower than the eutectic temperature (about 640 °C). Samples of each type were annealed for three different times—30 s, 60 s, and 5 min.

According to the evaluations of Fenske *et al.* [14] the characteristic infrared (IR) pattern should be recognized for thin films of thickness down to at least 10 nm, which makes the IR characterization even more sensitive than the conventional X-ray analysis.

In our samples the Mg_2Si phase is obviously in the form of precipitates, however the effective thickness of the phase is of the order of 50 nm as can be evaluated from Fig. 1. Thus we used the IR spectra as a standard of judgment whether the Mg_2Si phase is formed in our samples. In Fig. 2a–d the transmittance (T) spectra of samples fabricated with different doses of the implanted Mg ions are shown. The spectra were recovered at room temperature, using a Bohmem Fourier spectrometer, in the wavenumber range 200–400 cm^{-1}.

The frequency of the one IR active mode for the cubic Mg_2Si that crystallizes in the antifluorite structure, space group Fm3m, calculated by Baranek *et al.* [14] with the all-atomic-electron basis, is 272 cm^{-1}. The IR reflectance of bulk Mg_2Si single crystals was studied by McWilliams *et al.* [15]. The quantitative interpretation of the spectra gives for the infrared active mode frequency the value 8×10^{12} s^{-1} (about 277 cm^{-1}) which is in excellent agreement with the later theoretical calculations of Baranek *et al.* [14].

Strong absorption at 273–275 cm^{-1}, which can be attributed to a simple harmonic oscillator, is observed in the spectra of the samples implanted with D3 and D4, shown in Fig. 2c,d. A minimum, though not so sharp, is clearly resolved at almost the same wave number, 277–279 cm^{-1}, in the spectra of the samples implanted with D1 and D2 also, Fig. 2a and b. Sample-to-sample differences are expected and quite natural as the samples were prepared order different regimes. The different implantation doses imply different effective thicknesses of the Mg_2Si phase and thus—different transmittance values.

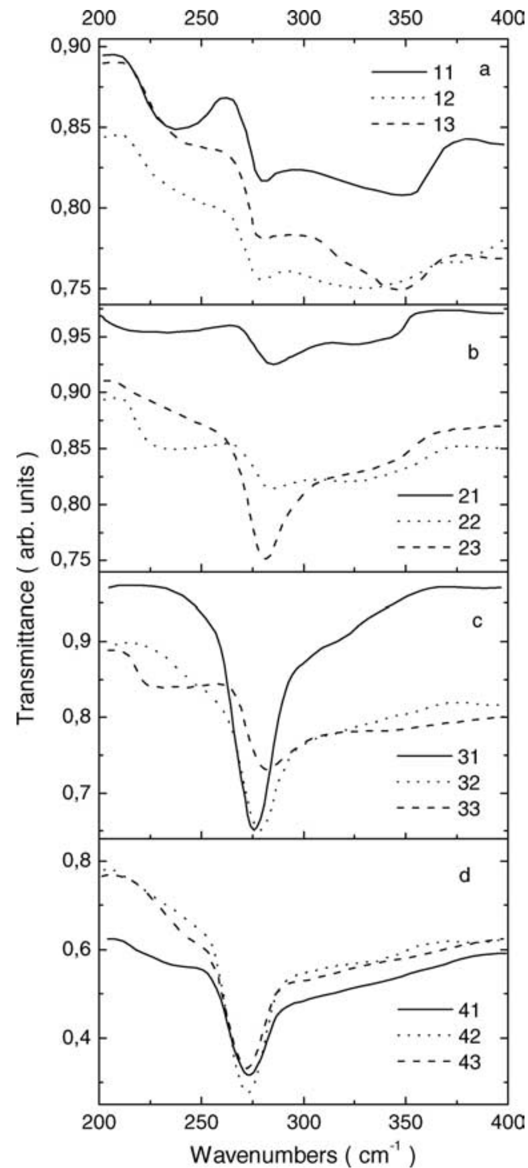

Figure 2 Infrared transmittance spectra of the samples, fabricated with four different implantation doses with Mg ions profiles shown in Fig. 1, and annealed for different times—1 as a second figure in the samples notation means 30 s, 2—60 s and 3—5 min. The first figure in the samples notation stands for the dose—1 for D1, 2 fot D2, 3 for D3 and 4 for D4.

The variation of the annealing time is supposed to lead to a change of the crystallites quality—the size, the lattice parameter uniformity, the stoichiometry and in this way to a change of the carrier concentration and the damping parameter. It is well known that these parameters most strongly influence the IR spectra behavior. The experimental IR spectra, shown in Fig. 2a–d indicate unambiguously the presence of the Mg_2Si phase in all of our samples. The wave number position of the well-observed minima in the T spectra at about 275 cm^{-1} coincides fairly well with the one obtained both by theoretical calculations and experimental investigations. It is worth noting that, as seen from Fig. 2, the lower the implanted dose, the stronger is the influence of the annealing time on the IR spectra behavior. While the spectra of the samples prepared with the highest dose, D4 (Fig. 2d), are almost identical, those of the samples implanted with lower doses differ significantly (Fig. 2a and b).

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