Thin film growth of semiconducting Mg_2Si by codeposition

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Ultrahigh vacuum evaporation of magnesium onto a hot silicon substrate (⩾200 °C), with the intention of forming a Mg_2Si thin film by reaction, does not result in any accumulation of magnesium or its silicide. On the other hand, *co*deposition of magnesium with silicon at 200 °C, using a magnesium-rich flux ratio, gives a stoichiometric Mg_2Si film which can be grown several hundreds of nm thick. The number of magnesium atoms which condense is equal to twice the number of *silicon* atoms which were deposited; all the silicon condenses while the excess magnesium in the flux desorbs. The Mg_2Si layers thus obtained are polycrystalline with a (111) texture. From the surface roughness analysis, a self-affine growth mode with a roughness exponent equal to 1 is deduced. © *1997 American Institute of Physics.* [S0003-6951(97)00409-9]

For decades, it has been known that Mg_2Si is a narrow-band-gap semiconductor, with an indirect band gap of 0.6–0.8 eV.[1,2] In spite of potential detector applications in the 1.2–1.8 μm infrared range relevant for optical fibers, thin film growth of Mg_2Si/Si heterostructures has received scant attention. The difficulty of forming Mg_2Si films, due to a low condensation coefficient and a high vapor pressure for magnesium, is probably the main reason that thin film studies are scarce.

Only a few such studies have been published. Chu *et al.*[3] reported that a magnesium film deposited at room temperature starts to react with a silicon substrate at a temperature as low as 200 °C, forming Mg_2Si. No experimental details of the solid state reaction were provided. Wittmer *et al.*[4] described the formation of Mg_2Si by pulsed laser annealing of *e*-gun-evaporated magnesium layers deposited onto Si(111). They found that crystallites of silicon were present in the polycrystalline silicide layer. Janega *et al.*[5] formed Mg_2Si by rapid thermal annealing of 100-nm-thick magnesium layers on Si(100). The magnesium was capped with 500 nm of aluminum to prevent it from evaporating during the reaction.

In this letter, we describe a method for obtaining Mg_2Si thin films by molecular beam epitaxy. The problem of a very low condensation coefficient for magnesium on silicon substrates was overcome by using a modest substrate temperature (200 °C) and by using *co*deposition of magnesium and silicon.

Magnesium (99.9% purity) and silicon (99.999% purity) were deposited using a ultrahigh vacuum evaporator (base pressure in the 10^{-11} Torr range) equipped with two *e*-guns. Calibration of the magnesium and silicon fluxes was accomplished using a quartz crystal monitor; typical deposition rates of 0.1–0.6 nm/s were used. As substrates, polished (111) and (001) silicon wafers were utilized. The wafers were cleaned using a dip into buffered oxide etch (10/1 NH_4F/HF) Followed by *in vacuo* annealing at 400 °C and a ''silicon-beam clean'' at 800 °C,[6] resulting in a sharp 7×7 reconstructed reflection high energy electron diffraction (RHEED) pattern for the (111), and the two-domain 2×1 pattern for the (001) substrates.

1.97 MeV $^4He^+$ backscattering and channeling measurements were made using scattering angles of 172° and 110°. Copper $K_\alpha(\lambda=0.154051$ nm) x-ray diffraction patterns were obtained in the θ–2θ geometry. The surface profile of the layers was measured by atomic force microscopy in noncontact mode.

For a first attempt to prepare Mg_2Si thin films, we chose reactive deposition of magnesium onto hot silicon substrates, based on its success with other silicides. Several tens of nanometers of magnesium were evaporated, at the following substrate temperatures: 200, 300, 400, and 500 °C. On none of the wafers could any accumulation of magnesium be observed. Since the re-evaporation rate of magnesium is calculated to be negligible compared to the nominal deposition rate,[7] it can be concluded that the condensation coefficient of magnesium on a silicon surface is practically equal to zero in the temperature range of 200–500 °C.

In the hope that a population of silicon adatoms present on the substrate surface would induce a condensation of the impinging magnesium atoms, we performed codeposition of silicon together with magnesium. A silicon flux corresponding to a silicon deposition rate on the order of 0.1 nm/s was used. A magnesium flux of 4 to 10 times this value was chosen, resulting in a quite magnesium-rich flux ratio. In all the codeposition growths, the substrate temperature was 200 °C, a temperature at which no magnesium accumulates during intended reactive deposition. This approach resembles the ''three-temperature method'' as developed by Freller and Günther.[8] Their analysis showed that there is a regime of flux

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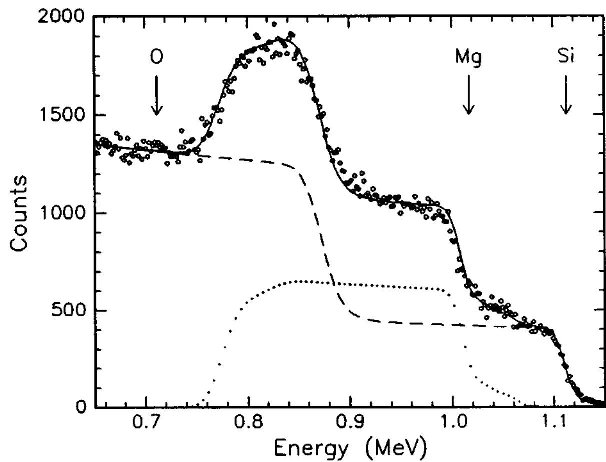

FIG. 1. 1.97 MeV $^4He^+$ backscattering spectra for a codeposited Mg_2Si on Si(111): (Open circles) random beam incidence; (solid lines) simulation; (dotted lines) magnesium, and (dashed lines) silicon part of the simulation. The scattering angle of the detected particles is 172°.

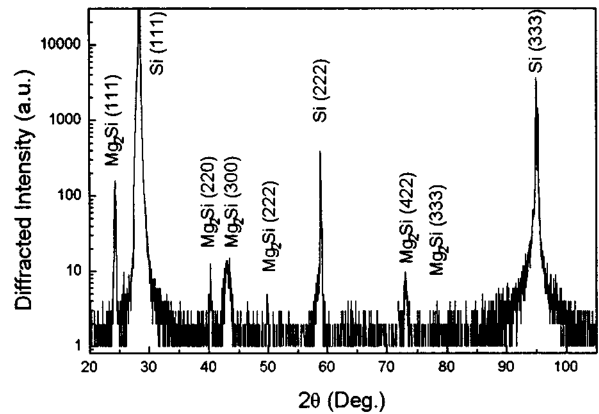

FIG. 2. X-ray diffraction pattern in the θ–2θ geometry for the Mg_2Si film shown in Fig. 1.

ratio and substrate temperature where a single-phase compound film can be deposited even though the incident fluxes are not in the stoichiometric ratio, provided the more volatile component is present in excess.

Coevaporation was successful, with the amount of Mg_2Si formed corresponding to the amount of silicon deposited. As an example, deposition of 25 nm silicon along with 96 nm magnesium (as measured with the quartz crystal oscillator) results in an 80-nm-thick Mg_2Si film. This Mg_2Si thickness of 80 nm corresponds to an accumulation of 26 nm silicon, in very good agreement with the nominal value. Apparently, no silicon is consumed from the substrate (to within the accuracy of our analytical techniques), despite the presence of excess magnesium. In contrast to the complete condensation of silicon, the Mg_2Si thickness of 80 nm also corresponds to a magnesium accumulation of only 58 nm, although 96 nm of magnesium was actually evaporated.

Thus, the use of the silicon flux increases the condensation coefficient of magnesium to a value such that two magnesium atoms condense for each silicon atom impinging on the substrate, while the excess magnesium desorbs. The value for the condensation coefficient of magnesium in the condition of excess magnesium flux is simply

$$\alpha_c = \frac{2j_{\mathrm{Si}}}{j_{\mathrm{Mg}}},$$

where j is the deposition flux. In other words, the condensation of magnesium is *self-regulating*.

Using this coevaporation technique, films with thicknesses of several hundreds of nm were grown. As an example, Fig. 1 shows the backscattering spectrum, together with a RUMP[9] simulation (taking a roughness of 30 nm into account, cf. infra) for a 600-nm-thick Mg_2Si film grown on Si(111). To assist in understanding the spectrum, the magnesium and silicon parts of the simulated backscattering spectrum are plotted as well. The simulation further indicates that, within the sensitivity of backscattering spectrometry, the stoichiometric composition of the film equals Mg/Si $=2/1$. In none of the Mg_2Si films, we have grown has any channeling been observed, implying that the layers are not epitaxial.

Figure 2 shows an x-ray diffraction pattern for the same codeposited film as shown in Fig. 1. The peak located at 24.24° is the $Mg_2Si(111)$ diffraction,[10] implying a (111) texture. While the (111) diffraction peak of the random powder pattern has an intensity of only 41% of the strongest peak, i.e., the (220) peak,[11] we observed predominant (111) peaks for all our layers. The (222) peak is also seen, as well as a weak (333) peak and diffraction peaks due to grains with a different orientation (Fig. 2). All Mg_2Si peak positions are in experimental agreement with the bulk lattice parameter of 0.63512 nm.[11] For both (111) and (001) substrate orientations, a (111) texture was always observed. An optical characterization of the Mg_2Si films thus obtained indicates an indirect band gap at 0.74 eV, plus direct transitions at 0.83 and 0.99 eV.[7]

The surface roughness of the Mg_2Si layers was studied with atomic force microscopy. Figure 3(a) shows a topographic micrograph of a 600-nm-thick layer, with a saturation roughness σ_t (see below) equal to about 30 nm. The contrast of the image is considerably enhanced when capturing a deflection image of the same part of the sample [Fig. 3(b)]. (On the other hand, the height scale information is no longer quantitative when utilizing the latter imaging mode.) From Fig. 3(b), a granular structure becomes clearly visible, suggesting a polycrystalline silicide. However, careful investigation shows that the grain distribution is not at all random. Many protuberances exhibit a tendency toward 6-fold symmetry throughout the scanned area, a typical morphology related to (111) texture. This further supports the conclusions drawn from x-ray diffraction measurements.

Since the measured roughness in general depends upon the sampling length, the root mean square (rms) roughness σ has been determined as a function of the scan length L measured in the surface plane. For each scan length, σ was averaged over measurements at 15 different positions on the sample surface.

As shown in Fig. 4, log(σ) varies linearly with log (L) over nearly three orders of magnitude, before saturation occurs. This behavior, i.e., $\sigma \sim L^H$, with H the roughness exponent, is typical for a self-affine growth mode.[12] From the

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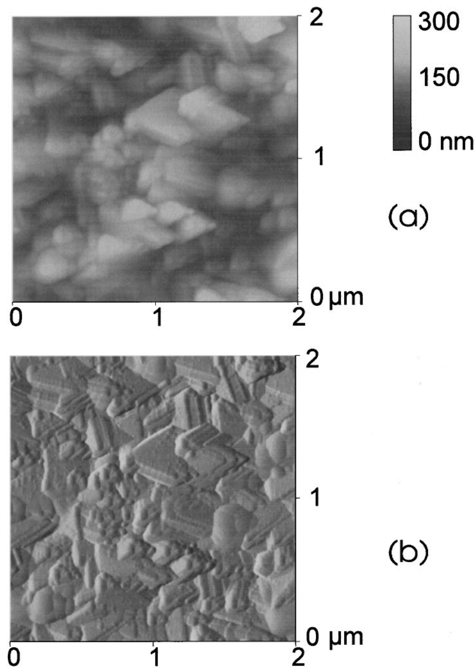

FIG. 3. Atomic force micrographs of the Mg_2Si layer shown in Fig. 1: (a) topographic image; (b) deflection image.

data in Fig. 4, $H=1.0\pm0.1$ and $H=0.9\pm0.1$ are deduced for a 600 and 80-nm-thick layer, respectively. Moreover, from the atomic force microscopy data (Fig. 4), it is observed that the saturation roughness σ_t increases with increasing thickness.

The value $H\approx 1$ is consistent with an atomistic model of 3D island growth, implying extensive surface diffusion. On the other hand, other growth models assuming a high degree of condensation (i.e., a large sticking coefficient) and only limited lateral diffusion (i.e., relaxation, which can be governed either by a potential difference in the gravitational field, a difference in surface chemical potential, the number of nearest neighbors, etc.)[13] generally predict much smaller roughness exponents, in the order of 0.3 to 0.5. We refer to Ref. 14 for a recent overview of these growth models.

From all these observations, a growth model for codeposited Mg_2Si can be deduced. The weak bonding of the magnesium atoms to the substrate (resulting in no magnesium accumulation during reactive deposition) allows a high surface mobility for magnesium adatoms, while they are on the substrate surface. This high surface mobility is evidenced by the roughness exponent $H=1$. The addition of a population of silicon adatoms, through codeposition, induces the condensation of magnesium adatoms, because the latter can bond more strongly to silicon adatoms, compared to less reactive silicon atoms occupying more fully coordinated sites (terrace, ledge, or even kink) of a vicinal surface. Since extensive surface diffusion is indispensable for reaction of magnesium with *all* silicon adatoms, the high surface mobility is a *necessary condition* to form a stoichiometric Mg_2Si film. Any magnesium left over, after all silicon adatoms are consumed, does not condense on the substrate. In other words, Mg_2Si growth is made possible by silicon induced condensation of magnesium, the mechanism of which is extensive surface diffusion.

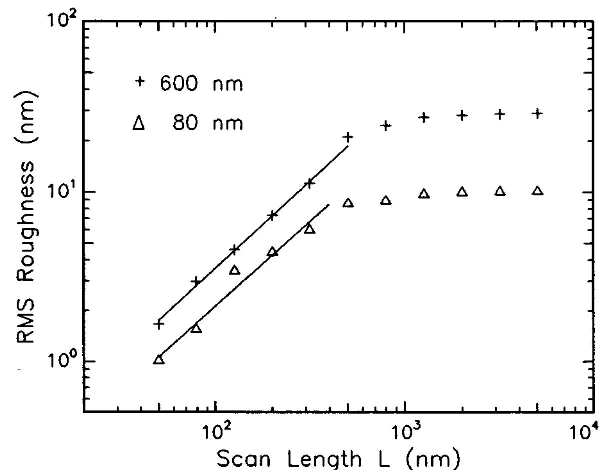

FIG. 4. rms roughness as a function of AFM scan length, for Mg_2Si films of two thicknesses on Si(111).

In summary, during reactive deposition of magnesium onto hot silicon substrates, no magnesium accumulates at substrate temperatures ⩾200 °C due to the very low condensation coefficient. On the other hand, polycrystalline films may be obtained at 200 °C using Mg–Si codeposition with a magnesium rich flux ratio. The amount of Mg_2Si which accumulates corresponds to the amount of deposited silicon; the excess magnesium does not condense. While the silicon condensation coefficient is unity, that of magnesium adjusts automatically to give a film of stoichiometric composition.

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[1] R. G. Morris, R. D. Redin, and G. C. Danielson, Phys. Rev. **109**, 1909 (1958).
[2] A. Stella and D. W. Lynch, J. Phys. Chem. Solids **25**, 1253 (1964).
[3] W. K. Chu, S. S. Lau, J. W. Mayer, H. Müller, and K. N. Tu, Thin Solid Films **25**, 393 (1975).
[4] M. Wittmer, W. Lüthy, and M. Von Allmen, Phys. Lett. A **75**, 127 (1979).
[5] P. L. Janega, J. McCaffrey, D. Landheer, M. Buchanan, M. Denhoff, and D. Mitchel, Appl. Phys. Lett. **53**, 2056 (1988).
[6] J. P. Becker, R. G. Long, and J. E. Mahan, J. Vac. Sci. Technol. A **12**, 174 (1994).
[7] J. E. Mahan, A. Vantomme, G. Langouche, and J. P. Becker, Phys. Rev. B (to be published).
[8] H. Freller and K. G. Günther, Thin Solid Films **88**, 291 (1982).
[9] L. R. Doolittle, Nucl. Instrum. Methods **9**, 344 (1985).
[10] Mg_2Si has a face-centered cubic CaF_2 (antifluorite) structure. A range of lattice parameters are reported in the literature, the most recent JCPDS card (Ref. 11) giving a value of 0.63512 (2) nm. There is no good lattice matching for epitaxial growth of Mg_2Si on silicon substrates.
[11] *Powder Diffraction Data File* (JCPDS International Center for Diffraction Data, Swarthmore, PA, 1990), Card 35-773 (unpublished).
[12] J. Krim, I. Heyvaert, C. Van Haesendonck, and Y. Bruynseraede, Phys. Rev. Lett. **70**, 57 (1993).
[13] D. E. Wolf and J. Villain, Europhys. Lett. **13**, 389 (1990).
[14] A.-L. Barabási and H. E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge University Press, Cambridge, 1995).

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