

Semiconducting Mg₂Si thin films prepared by molecular-beam epitaxy

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Mg₂Si is a semiconductor with a band gap previously reported to be in the range 0.6–0.8 eV. In spite of potential optoelectronic applications in an important infrared range, the growth of Mg₂Si thin films on silicon substrates has received scant attention. This may be due to the difficulty of preparing Mg₂Si in thin-film form. We find that intended *reactive* deposition of magnesium onto a silicon substrate, at temperatures from 200 to 500 °C, results in no accumulation of magnesium. However, *codeposition* of magnesium with silicon at 200 °C, using a magnesium-rich flux ratio, gives a stoichiometric Mg₂Si film. The amount of magnesium which accumulates is determined by the total amount of *silicon* which was codeposited; the excess magnesium in the flux does not condense. Measurements of the optical transmittance of thin films thus obtained reveal an absorption edge. Extraction of the absorption coefficient from the data, and analysis of its energy dependence, suggest an indirect band gap of ~0.74 eV, plus direct transitions at ~0.83 and ~0.99 eV. [S0163-1829(96)09547-1]

INTRODUCTION

It has been known for at least 40 years that Mg₂Si is a narrow-band-gap semiconductor, with the reported band-gap values in the range 0.6–0.8 eV. Photoconductivity in bulk samples was demonstrated as early as 1964.¹ This material's potential for providing optoelectronic functions on silicon chips should have attracted at least some exploratory work, because if it possesses the desirable properties, it could lend itself to the creation of detectors (if not sources) in the important 1.2–1.8 μm range of optical fibers. However, the only publication of which we know that deals with electronic applications of Mg₂Si thin films is an exploration of possible low-resistivity contacts to *n*-type silicon.²

The value of the forbidden energy gap is not precisely known. Morris *et al.*³ measured the temperature dependence of resistivity of bulk single crystals; from the thermal activation energy in the intrinsic regime they found a band gap of 0.78 eV. The authoritative work seems to be from the 1960's—the most complete investigation of optical properties that we know is by Koenig *et al.*⁴ However, they were unable to fit a theoretical expression to the absorption coefficient data and so no value for the gap was determined (their absorption edge was in the vicinity of 0.65 eV). Stella and Lynch¹ published their photoconductivity results in 1964, with a photon energy threshold at about 0.6 eV. Folland⁵ wrote that the “[experimental] electrical gap is 0.77 eV, the optical gap is about 0.67 eV, and the photoconductive gap is 0.65 eV.” Au-Yang and Cohen⁶ determined a band gap of ~0.6 eV from measurements of the imaginary part of the dielectric function. Teheda and Cardona⁷ gave a value of 0.73 eV for the “thermal band gap.”

There does seem to be unanimous agreement in the literature on the *type* of energy gap. Koenig *et al.*⁴ state that “the absorption edge appears to be due to indirect transitions.” Folland,⁵ and all others who have reported band-structure

calculations (Lee,⁸ Au-Yang and Cohen,⁶ Tejada and Cardona⁷), predict that the minimum energy transition is indirect. Tejada and Cardona⁷ point out that Mg₂Si, with its antiferroite structure, is “isoelectronic to the germaniumlike semiconductors, and since they have the same translation lattice their band structures are very similar . . . The top of the valence band is at Γ (like in the germanium-type semiconductors) while the lowest conduction band minimum seems to be at X (like in silicon).”

The early experimental work mentioned above was performed with bulk single-crystal samples, rather than thin films. Indeed, we find that Mg₂Si film formation is difficult, due to a low condensation coefficient, and a high vapor pressure, for magnesium. This may be one reason that thin-film studies of this silicide are scarce.

We will summarize here the film preparation aspects of all the thin-film studies of which we are aware, after doing two computerized literature searches and informally collecting articles over several years: (1) Chu *et al.*⁹ reported that “when a magnesium film reacts with a silicon substrate it forms Mg₂Si at a temperature as low as 200 °C and magnesium atoms are the predominant moving species;” no experimental details of the film deposition or solid-state reaction were provided. (2) Tejada and Cardona⁷ prepared polycrystalline films by sputtering onto room-temperature substrates (no other details provided). (3) Wittmer *et al.*¹⁰ described the formation of Mg₂Si by pulsed laser annealing of *E*-gun-evaporated magnesium layers deposited onto 111 silicon. They stated that the “laser pulse melts the metal and a thin layer of the underlying silicon,” and found that polycrystallites of silicon were present in the polycrystalline silicide layer. (4) Janega *et al.*² formed Mg₂Si by reaction of 1000-Å-thick magnesium layers with 100-oriented silicon substrates; the magnesium was capped with 5000 Å of aluminum before the reaction. Both metals had been vacuum evaporated and the reaction was induced with a rapid thermal

annealing system. (5) Boher *et al.*¹¹ prepared completely amorphous W/Mg₂Si multilayers by radio-frequency (RF) diode sputtering, using a Mg₂Si target. The substrates were (111) silicon wafers, or glass, presumably held near room temperature. They chose this multilayer system over W/Mg because "it is difficult to deposit magnesium as a uniform thin film due to its low melting point and high vapor pressure. In this respect, magnesium silicide seems more attractive." They found it necessary to utilize a particularly low sputtering power in order to avoid decomposition of the Mg₂Si target; the necessarily low deposition rate was a drawback for the fabrication of x-ray mirrors.

We describe in this article a method for obtaining Mg₂Si thin films by molecular beam epitaxy (MBE). The problem of a very low condensation coefficient for magnesium was overcome by utilizing a modest substrate temperature (200 °C) plus the codeposition mode. Optical characterization of the Mg₂Si films thus obtained suggests that the band-gap value is ~0.74 eV, and that it is indirect in nature.

BACKGROUND: THE Mg₂Si PHASE; CRYSTALLOGRAPHIC DATA

Below 637.6 °C (an eutectic temperature), the equilibrium phases in the Mg-Si phase diagram are (1) the terminal magnesium solid solution, with a maximum solid solubility of 0.003 at. % silicon, (2) the stoichiometric compound Mg₂Si, and (3) the terminal silicon solid solution, with negligible solid solubility of magnesium.¹²

Mg₂Si crystallizes in the face-centered-cubic CaF₂ (anti-fluorite) structure, with space group *Fm*3*m*. A range of lattice parameters may be found in the literature, from 6.338 Å (Ref. 13) to 6.39 Å.² The most recent JCPDS card¹⁴ gives a value of 6.351 19 Å. There appears to be no good lattice matching for epitaxial growth of Mg₂Si on silicon substrates.

EXPERIMENTAL PROCEDURES

Magnesium was deposited onto silicon wafer substrates using an ultrahigh vacuum *E*-gun evaporator (base pressure in the 10⁻¹¹ torr range). The *E* gun provides a magnesium flux at the substrate corresponding to a deposition rate of typically 2–6 Å/s. The magnesium source material was a pellet of 3*n* purity (the highest that was commercially available). In coevaporation experiments, silicon (5*n* purity) was deposited using a second *E* gun. Calibration of the magnesium and silicon fluxes was accomplished using a quartz crystal monitor controlled by a Leybold-Inficon Sentinel III deposition controller.

The substrates were polished 111 and 001 silicon wafers. The 111 substrates, prior to magnesium evaporation, exhibited a sharp 7×7 reconstructed reflection high-energy electron diffraction (RHEED) pattern, and the 001 substrates, the two-domain 2×1 pattern. These reconstructed surfaces had been obtained with the following cleaning procedure: an initial dip of the wafer into buffered oxide etch (10/1 ammonium fluoride/HF) followed by *in vacuo* annealing at 400 °C and a "silicon-beam-clean" at 800 °C.¹⁵

For materials characterization of the thin films, ⁴He⁺ backscattering [Rutherford backscattering spectrometry

(RBS)] and channeling measurements were made with a 1.97-MeV beam. Scattering angles of 172° and 110° were used. Copper *K*α x-ray diffraction patterns were obtained in the θ -2 θ geometry.

For film transmittance measurements, from which the optical absorption coefficient as a function of photon energy was derived, thin-film samples were front-side illuminated with a quartz-halogen source, grating monochromator (bandwidth ~12.8 nm, or ~0.01 eV at 1 μm), and order-sorting filters. The incident- and transmitted-light intensities were measured with a HgCdTe photoconductive detector. Phase-sensitive detection was accomplished with an optical chopper and lock-in amplifier.

Mg₂Si THIN-FILM FORMATION BY MOLECULAR-BEAM EPITAXY

To prepare Mg₂Si thin films, we first tried reactive deposition of magnesium onto hot 111-oriented silicon substrates. Several hundred angstroms of magnesium were evaporated, using each of the following substrate temperatures: 200, 300, 400, and 500 °C. *In none of these attempts at intended reactive deposition was there a measurable accumulation of magnesium*; the substrates after each experiment remained bare by visual inspection, by conventional x-ray diffraction, and by MeV ⁴He⁺ Rutherford backscattering spectroscopy. (However, a fractional monolayer of adsorbed magnesium probably existed on these substrate surfaces—see Appendix.)

Why did no film—either pure magnesium or magnesium silicide—accumulate during these attempts at reactive deposition? To understand this, we calculate what the net deposition rate of magnesium should have been, estimating a reevaporation rate from the vapor pressure of magnesium at the lowest substrate temperature utilized, 200 °C (assuming complete thermal accommodation of the incident particles). The net growth velocity (condensation rate minus reevaporation rate, in Å/s) is given by

$$v_n = \frac{\alpha_c j - P/\sqrt{2\pi mkT}}{n_f}, \quad (1)$$

where α_c is the condensation coefficient, j is the deposition flux, P is the thermal equilibrium vapor pressure at the substrate temperature T , m is the atomic mass (of magnesium), k is Boltzmann's constant, and n_f is the atomic density (of magnesium). The second term in the numerator is actually the impingement rate expression from the kinetic theory of gases.¹⁶ By the principle of microscopic reversibility it is also the emission, or free evaporation, flux from a magnesium surface at the same temperature. The numerator is thus the condensation flux minus the reevaporation flux; dividing by atomic density of magnesium gives the net growth velocity.

At 200 °C the thermal equilibrium vapor pressure of magnesium is about 10⁻⁷ torr.¹⁶ This corresponds to a reevaporation (actually, sublimation) rate from a magnesium surface (using $m = 24.3$ amu and $n_f = 0.0430$ Å⁻³) of 0.0760 Å/s. This reevaporation rate is negligible compared to the nominal deposition rate of several Å/s provided by the *E*-gun evaporator. Hence, the condensation coefficient in Eq. (1) must be zero.

We tried codeposition of silicon together with magnesium (the molecular beam epitaxy deposition mode) in the hope that the silicon adatoms present on the substrate surface would induce a condensation of the impinging magnesium atoms. A silicon flux corresponding to a silicon deposition rate on the order of 1 Å/s was used. The magnesium flux was chosen to be 4–10 times this value in various growths, resulting in a quite magnesium-rich flux ratio. In all the MBE growths, the substrate temperature was 200 °C. This approach resembles the “three-temperature method” as developed by Freller and Günther.⁷ Their analysis showed that there is a regime of flux ratio and substrate temperature where a compound film “can be deposited even though the incident rates are not in the stoichiometric ratio and the more volatile component is present in excess.”

Molecular beam epitaxy was successful, and the amount of Mg₂Si film formed corresponds to the amount of silicon deposited. As an example, we will present in the next section a RBS spectrum for an 810-Å-thick Mg₂Si film. This thickness corresponds to an accumulation of 590 Å of magnesium, although 955 Å of magnesium was actually evaporated. The Mg₂Si thickness of 810 Å also corresponds to a silicon accumulation of 255 Å. In contrast to the behavior of the magnesium, the amount of silicon which was evaporated during the film growth (244 Å, as measured with the quartz crystal oscillator) corresponds closely (within the error of backscattering spectrometry) to the amount which is contained within the Mg₂Si film (255 Å).

During and after the MBE film growths, faint and diffuse polycrystalline rings were seen on the RHEED screen, indicating a polycrystalline microstructure. This uninspiring pattern actually plays an important role. It is, we believe, the signature of polycrystalline Mg₂Si. Other unique RHEED patterns had been observed—during the attempts at reactive deposition, a Si(111)-3×1 streak pattern due to an adsorbed magnesium layer, and during room-temperature deposition of magnesium onto Si(111), a spotty streak pattern indicating a rough, epitaxial, pure magnesium layer. These other patterns are discussed in the Appendix.

Within the accuracy of our deposition controller, the silicon condensation coefficient appears to be unity. Furthermore, the use of the silicon flux increases the condensation coefficient of magnesium to a value such that two magnesium atoms may condense for each silicon atom impinging on the substrate. The excess magnesium desorbs. The value for the condensation coefficient of magnesium in the condition of excess magnesium flux is simply

$$\alpha_c = \frac{2j_{\text{Si}}}{j_{\text{Mg}}} \quad (2)$$

Thus, the condensation of magnesium is self-regulating.

COMPOSITIONAL ANALYSIS AND PHASE IDENTIFICATION FOR MBE-GROWN FILMS

In Fig. 1 we show a representative MeV ⁴He ion backscattering spectrum for a film grown on Si(111), together with a RUMP¹⁸ simulation of the spectrum. As mentioned in the previous section, the RUMP simulation suggests a film thickness of 810 Å. Furthermore, the simulation indicates that the film composition is very close to ideal because the

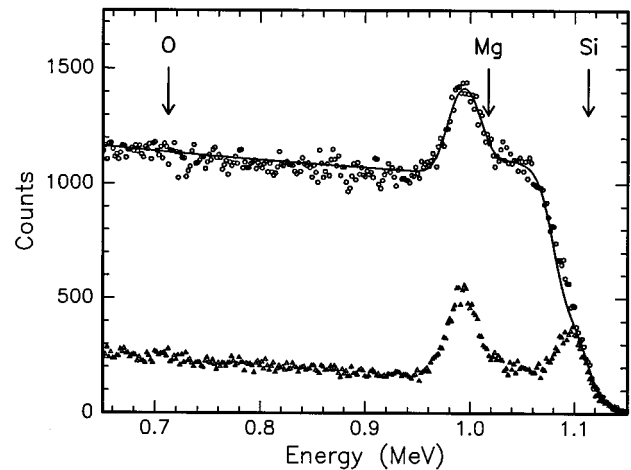


FIG. 1. 1.97-MeV ⁴He⁺ backscattering spectra for a MBE-deposited Mg₂Si film: random (○) and 111-aligned (△) beam incidence. The scattering angle of detected particles is 172°. The RUMP (Ref. 20) simulation (solid line) indicates a stoichiometric composition and a film thickness of 810 Å.

assumed stoichiometric composition (Mg/Si=2/1) matches the shape of the experimental spectrum quite well. Epitaxy is not indicated; no channeling has been observed in any Mg₂Si film we have grown.

In Fig. 2, we show an x-ray diffraction pattern for another MBE-grown film. It is 480 Å of Mg₂Si deposited onto Si(001). The peak at 24.24° is identified as the Mg₂Si 111 reflection (predicted position 24.25°), implying a 111 texture. The 222 peak is also seen, and the 333 peak may be inferred from the shoulder on the strong Si 004 substrate peak. In addition, there is a Mg₂Si 220 reflection. The Mg₂Si peak positions are in experimental agreement with the JCPDS lattice parameter of 6.351 19 Å. We observed no significant effect of silicon substrate orientation (111 vs 001) on the growth and properties of the Mg₂Si films. The 111 texture was always indicated. Other phenomena relating to

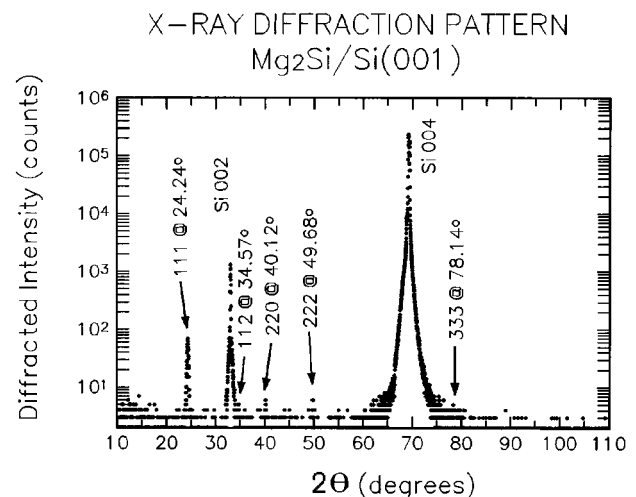


FIG. 2. X-ray diffraction pattern in the θ - 2θ geometry for a film grown on Si(001). Theoretical peak positions and their Miller indices are indicated with vertical labels.

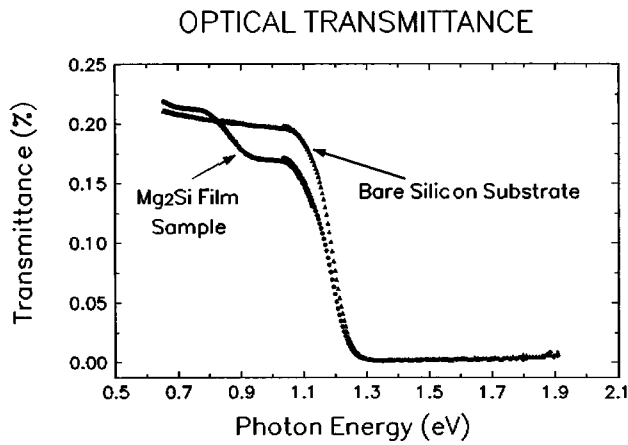


FIG. 3. Optical transmittance of an Mg₂Si film sample, together with that of a bare silicon wafer substrate.

Mg₂Si film growth are summarized in the Appendix.

OPTICAL ABSORPTION EDGE

The Mg₂Si films thus prepared exhibit optical transparency at sufficiently long wavelengths, and an absorption edge. Shown in Fig. 3 is the transmittance of a 5770-Å-thick Mg₂Si film, plus data for a silicon substrate identical to the one on which the film was grown. (The silicon substrates had only one side which was polished, the other side being "bright-etched." As a result, the silicon transmittance at photon energies below the silicon absorption edge was below the expected value of ~0.54, due to diffuse reflectance at this nonpolished back surface.) The silicon absorption edge near 1.1 eV is apparent in both data sets.

Between ~0.8 and 1.2 eV, the transmittance of the Mg₂Si sample markedly decreases, and over most of this range it is much less than that of the bare substrate. This appears to be a manifestation of the fundamental interband absorption of Mg₂Si. We will estimate the optical absorption coefficient of Mg₂Si from this data using the following rudimentary optical model.

Assumptions: (1) We will ignore multiple internal reflections in the film. While interference fringes are actually

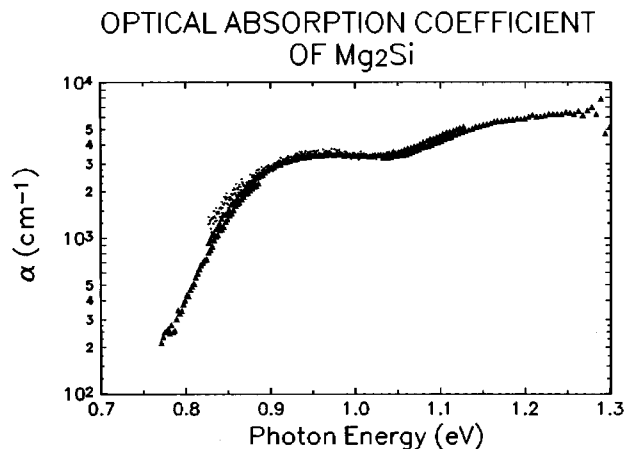


FIG. 4. The optical absorption coefficient of Mg₂Si, derived from Fig. 3.

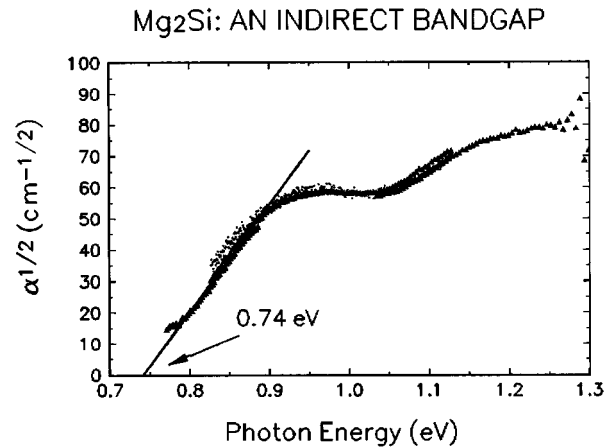


FIG. 5. Indication of an indirect band gap of ~0.74 eV, from a portion of the data (0.80–0.89 eV) of Fig. 4. The small dots are a separate data set not used in the band-gap determination.

present in the film data of Fig. 3, they are minor compared to the strong absorption effect. (The fact that below ~0.8 eV the Mg₂Si sample's transmittance is greater than that of the bare substrate is actually due to destructive interference of light reflected from the front and back surfaces of the film. We estimate an index of refraction for Mg₂Si, 3.67, which is slightly higher than that of silicon, 3.42, from interference extrema observed below 0.5 eV in other data sets.) (2) We will assume that the indices of refraction of Mg₂Si and silicon are constant over the narrow energy range of interest in this paper; this implies that the reflectances of the various interfaces are also constant. Again, any variation of the indices should be minor in comparison to the strong absorption effect in Mg₂Si. (3) We will ignore light absorption by the silicon substrate, because even in the very limited range where it does noticeably occur, the effect of silicon absorption is removed from the data in the analysis procedure which follows.

Let the front surface reflectance of the film be R_f , the reflectance of the film-substrate interface be R_i , that for light exiting the backside of the substrate be R_b , and that of the front surface of a bare substrate be R_s . The transmittance of the sample is

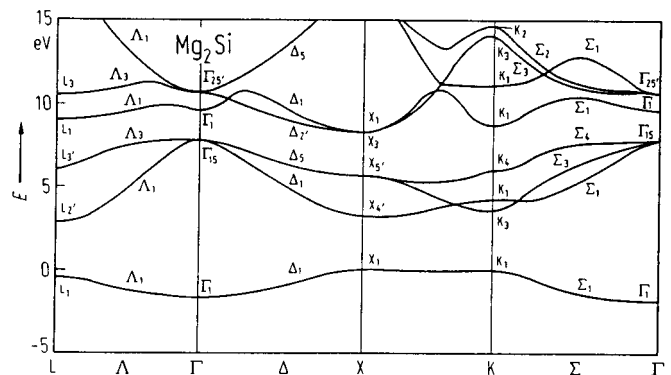


FIG. 6. A representative band structure for Mg₂Si, calculated according to the nonrelativistic pseudopotential method (Ref. 13).

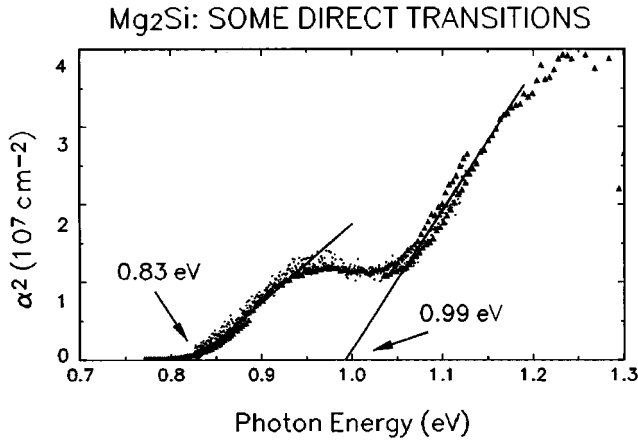


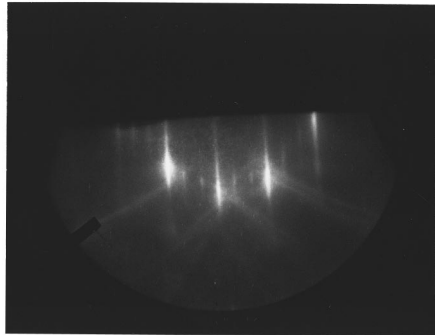
FIG. 7. Higher-energy direct transitions are indicated at ~ 0.83 and ~ 0.99 eV.

$$T \approx (1 - R_f) e^{-\alpha d} (1 - R_i) (1 - R_b), \quad (3)$$

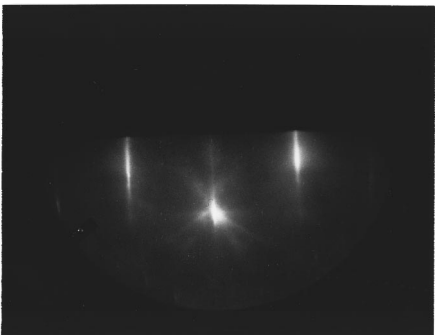
where d is the film thickness and α is the optical absorption coefficient of the film.

The transmittance of the bare substrate (T_{Si}) is $(1 - R_s)(1 - R_b)$. We will use this result to estimate the optical absorption coefficient from the data, by normalizing the transmittance of the film sample to that of the bare substrate:

$$\frac{T}{T_{Si}} \approx \frac{(1 - R_f)(1 - R_i)}{1 - R_s} e^{-\alpha d}. \quad (4)$$



(a)



(b)

FIG. 8. 3×1 RHEED patterns obtained during attempted reactive deposition of magnesium onto Si(111) at a substrate temperature of 300°C . The incident beam directions are (a) along Si $\langle 110 \rangle$ and (b) along Si $\langle 112 \rangle$.

Thus, the absorption coefficient may be calculated from the data using

$$\alpha = \frac{1}{d} \ln \left(\frac{1 - R_s}{(1 - R_f)(1 - R_i)} \frac{T_{Si}}{T} \right). \quad (5)$$

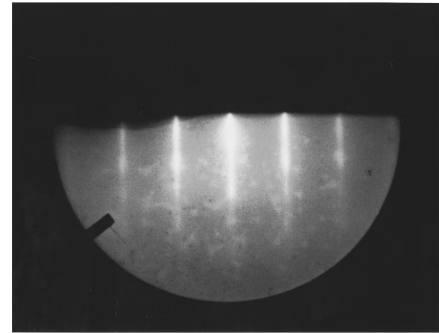
Based on assumptions stated above, the reflectance term in Eq. (5) will be assumed to be constant. We estimate its value as 1.05 from T/T_{Si} below the absorption edge of Mg₂Si.

The optical absorption coefficient of Mg₂Si is plotted in Fig. 4 as a function of photon energy. (Some additional data from a repetition of the measurement in the range 0.8–1.1 eV, which had not been shown in Fig. 3, was added.)

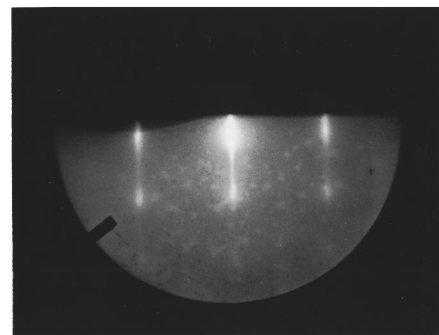
To determine the value and type of forbidden energy gap from this data, the absorption coefficient was replotted both as $\alpha^{1/2}$ and as α^2 versus photon energy. If $\alpha^{1/2}$ is a linear function of photon energy, the band gap is indirect while if α^2 is linear, it is direct; in either case the intercept with the photon energy axis indicates the band-gap value.¹⁹

Figure 5 suggests that the minimum energy transition is indirect, with a band-gap value near 0.74 eV. The straight line shown represents a linear regression curve fitting to data points between 0.80 and 0.89 eV. In Fig. 6 we present a representative band-structure calculation.¹³ The Γ_{15-X_3} (or Γ_{15-X_1}) transition would be the indirect transition found. The relatively low values of α where it seems to plateau (i.e., the mid- 10^3 range) are typical of an indirect gap.

Now, the structure in the absorption coefficient curve of Fig. 5 is more than can be explained by a single indirect transition. Indeed, the two linear ranges in Fig. 7 suggest that there are two higher-energy direct transitions, near 0.83 and 0.99 eV. (The data points used to construct these two lines



(a)



(b)

FIG. 9. RHEED patterns obtained after room-temperature deposition of 943 \AA of magnesium onto Si(111). The incident beam directions are (a) along Si $\langle 110 \rangle$ and (b) along Si $\langle 112 \rangle$.

are in the ranges 0.85–0.94 and 1.09–1.18 eV.) The intercepts might correspond to the $\Gamma_{15}-\Gamma_1$ and $\Gamma_{15}-\Gamma'_{25}$ transitions of the above band structure, which are the lowest energy direct transitions which are theoretically predicted. By contrast, Au-Yang and Cohen⁶ found a strong threshold in the energy spectrum of the imaginary part of the dielectric function at 2.0 eV, which they attributed to the direct transitions at Γ , because it was in excellent agreement with the theoretical value. A resolution of this point of disagreement will require further research.

We believe that these absorption transition energy values, particularly the direct ones, should be regarded as tentative. The reader who closely examines Figs. 5 and 7 will see that which points to use is a matter of judgment. Furthermore, it is a fact that some data points were utilized in the demonstration of *both* the indirect band gap *and* the lower-energy direct transition. Finally, our assumption of no interference effects could introduce some error; they could be present to some small degree and if so, would shift the intercept values.

SUMMARY AND CONCLUSIONS

Reactive deposition of magnesium onto hot silicon substrates, based on its success with other silicides, would seem a simple and effective method for obtaining Mg_2Si thin films as well. However, the condensation coefficient is so low that no magnesium accumulates at substrate temperatures $\geq 200^\circ\text{C}$.

On the other hand, polycrystalline films may be obtained at 200°C using molecular beam epitaxy with a magnesium-rich flux ratio. The amount of Mg_2Si which accumulates corresponds to the amount of silicon deposited; 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.

Mg_2Si thin films thus obtained were found to possess an indirect band gap in the vicinity of 0.74 eV. This value is within the range of previously reported experimental values, and the type is in agreement with all band-structure calculations. Direct, higher-energy transitions were also observed, near 0.83 and 0.99 eV. These direct transitions are also predicted by the theoretical calculations, but higher energies were expected.

With a view to optoelectronic applications of Mg_2Si thin films, it is disappointing that the indirect band gap seems confirmed, because a direct material is preferred for light emitters. However, band-gap engineering has already shown that it is impossible to predict advances, or be certain of limitations, in this area.

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APPENDIX: RELATED GROWTH PHENOMENA OBSERVED DURING ATTEMPTS AT MAGNESIUM SILICIDE FILM FORMATION

1. Magnesium adsorption

During the experiments on reactive deposition of Mg_2Si on Si(111), the initial 7×7 RHEED pattern was quickly

transformed to the 3×1 pattern of Fig. 8 as soon as the magnesium flux was started. This pattern is in extreme contrast to the diffuse rings observed for polycrystalline Mg_2Si . By 3×1 we mean that third-order streaks appeared with incident RHEED beam along Si $\langle 110\rangle$, while along Si $\langle 112\rangle$, the only streaks present had the fundamental spacing of silicon. At 500°C , the 3×1 reverted instantaneously to the familiar 7×7 as soon as the magnesium flux was turned off. At the lower temperatures, it persisted for longer times (a few seconds at 400°C to at least a few hours at 200°C). We hypothesize that this new RHEED pattern, and the new 111 surface mesh which caused it, were due to an adsorbed layer of magnesium.

2. Room-temperature epitaxy of magnesium

Magnesium was evaporated onto Si(111) wafers nominally at room temperature. The RHEED pattern after deposition consisted of spotty streaks, as shown in Fig. 9 for a deposit of 950 Å (as measured by RBS). An epitaxial alignment of the film is indicated, with the *c* axis of hexagonal magnesium being parallel to Si $\langle 111\rangle$. The epitaxial relationship is

$$\text{Mg}(0001)/\text{Si}(111) \quad \text{with} \quad \text{Mg}(1000)\parallel\text{Si}(110).$$

X-ray diffraction confirmed that the Mg(0001) planes are parallel to the Si(111) planes, by the dominant presence of the Mg 0002 peak.

This epitaxy was made possible by a lattice matching that is of poor quality. Using a magnesium “*a*” lattice parameter of 3.2094 Å (Ref. 20) and a Si(111) surface mesh parameter of 3.840 Å,¹⁵ the room-temperature mismatch is -16% , for a common unit mesh area of 13 \AA^2 . Since we observed no channeling effect, the crystalline quality of the room-temperature-deposited epitaxial magnesium is probably poor.

There was some reactive character to these magnesium depositions—a very small amount of the Mg_2Si phase was suggested by the presence of its 300 peak in the x-ray diffraction pattern of this sample (not shown). RBS analysis indicated about 10 at. % silicon in the nominally magnesium film.

3. Possible reactive deposition of magnesium

There may be a substrate temperature window below 200°C in which reactive deposition of magnesium, to form Mg_2Si by reaction with the silicon substrate, is feasible. Evaporation of magnesium onto a 111-oriented substrate held at 140°C gave a RHEED pattern that was neither that of epitaxial magnesium metal nor the adsorbed magnesium layer, but rather diffuse rings which are typical of polycrystalline Mg_2Si . X-ray diffraction revealed Mg_2Si 111 and 300 peaks which were much weaker than might be expected from the nominal 1000 Å of magnesium which had been evaporated.

4. Possible solid-phase reaction of an epitaxial magnesium layer with a silicon substrate

As discussed in the Appendix, an epitaxial magnesium layer is obtained by evaporating magnesium onto a (111)

substrate held at room temperature. Upon heating *in vacuo* to 200 °C, the RHEED pattern was converted from the strong streaks characteristic of epitaxial magnesium to the weak, diffuse, polycrystalline rings typical of Mg₂Si. With further annealing, the rings persisted to about 600 °C, at which point

the film sublimated, leaving a bare substrate. Boher *et al.*¹¹ stated without reference that “magnesium silicide is known to decompose to magnesium and silicon at about 600 °C under vacuum.” Silicide formation by solid-phase reaction was not pursued further in our work.

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