

Volatile metal-oxide incorporation in layers of GaAs, Ga_{1-x}Al_xAs and related compounds grown by molecular beam epitaxy

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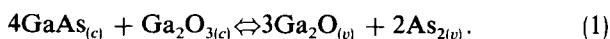
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A model is presented which relates the observed effects of substrate temperature and growth flux magnitudes upon layer quality to the presence of volatile oxides and the thermodynamics of the formation of nonvolatile oxides on the growth surface. A means for reducing oxide contamination is presented and the consequent benefits explored.

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Molecular beam epitaxy (MBE) of gallium arsenide and related compounds is successful, in part, owing to the relative volatility of arsenic. This enables near-stoichiometric growth, and hence good crystal quality, for relatively large disparities between the group-III and group-V fluxes. For a variety of considerations, however, not the least of which is the longevity of the arsenic charge, one would like to grow at as close to unity flux ratios as possible. This, owing to arsenic's volatility, requires low substrate temperatures. For throughput reasons, one would like to grow at high rates. Unfortunately, both low substrate temperature and high growth rates, specifically high arsenic pressure, yield crystals of poor electrical and optical properties.^{1,2} The minimum substrate temperature for GaAs is about 480°C (Refs. 1-5). For Ga_{1-x}Al_xAs with x > 0.1, the substrate must be maintained at 650-700°C.⁶ Growth rates are limited to about 1 μm/h, with the best V-III flux ratios at about 2:1.^{1,6} In this letter we develop a volatile oxide model which predicts these observations, as well as others. For example, magnesium has been shown^{3,4} to have a doping efficiency of 10⁻⁵ in gallium arsenide, but significantly higher in Ga_{1-x}Al_xAs. Also, As₂ proves to be a superior flux to As₄ for the growth of GaAs.⁸

We can explain these effects by examining the following equilibrium:



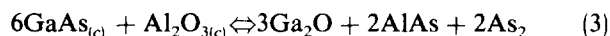
Ga₂O is a readily observed species whose primary source is the gallium oven, but with time is easily observed in the background spectrum. As₂ is the growth flux, we will treat the case of As₄ later. GaAs_(c) represents the crystal surface, and Ga₂O₃ is the nonvolatile oxide that we wish to avoid forming. Using Cho and Arthur's⁵ data for the dissociation of GaAs, and Cochran and Foster's⁷ data for the disproportionation of Ga₂O₃, we derive an expression for the maximum allowable pressure of Ga₂O, in atmospheres, in terms of the As₂ pressure and the substrate temperature:

$$\log P_{\text{Ga}_2\text{O}_{\text{max}}} = 17.52 - 2.8 \times 10^4/T - \frac{2}{3} \log P_{\text{As}_2} \quad (2)$$

Equation 2 is plotted in Fig. 1. For GaAs, there are three lines, each representing a different As₂ pressure. Each line defines, for that pressure, the substrate temperature and Ga₂O pressure that causes the equilibrium to shift from left to right. Above and to the right of the line, formation of

Ga₂O₃ is favored; below and to the left results in the rejection of Ga₂O from the surface. It is likely that if Ga₂O₃ is formed, it will be incorporated in the lattice as a defect. We propose that this is precisely the mechanism by which high arsenic pressures and low substrate temperatures produce layers of poor electrical and optical properties. Referring to Fig. 1, for the Ga₂O pressure of 1.5 × 10⁻¹⁰ atm that we had in our system and an As₂ pressure of 10⁻⁷ atm (about 1 μm/h) we find that we need a minimum substrate temperature of 600°C to avoid forming Ga₂O₃.

For Al_xGa_{1-x}As, one would expect the situation to get worse, and it does. Using the equilibrium



and using Hoch and Hinge's⁹ data for AlAs, we derive the equation

$$\log P_{\text{Ga}_2\text{O}_{\text{max}}} = 13.26 - 2.5 \times 10^4/T - \frac{2}{3} \log P_{\text{As}_2} \quad (4)$$

This equation is also summarized in Fig. 1. Thus for a given substrate temperature the allowable Ga₂O pressure is low-

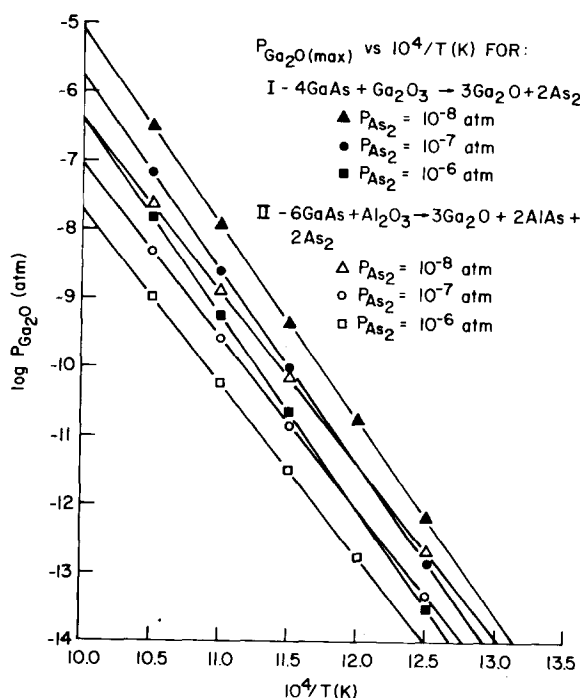
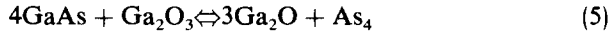


FIG. 1. Maximum allowable Ga₂O pressure vs reciprocal temperature for As₂ over (I) GaAs and (II) Al_xGa_{1-x}As.

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ered by about an order of magnitude. For our system's Ga_2O pressure, the required substrate temperature is about 630°C .

Let us now treat the case where an elemental arsenic source is used. Using Cho and Arthur's⁵ data for As_4 over GaAs , we find for



that

$$\log P_{\text{Ga}_2\text{O}_{\text{max}}} = 14.78 - 2.35 \times 10^4/T - \frac{1}{3} \log P_{\text{As}_4}. \quad (6)$$

This appears to indicate, at least at lower substrate temperatures, a significant improvement over As_2 . But the fact is that a high As_4 flux greatly perturbs the GaAs equilibrium, and the crystalline surface will quickly convert to As_2 all of the As_4 that adheres to it. The consequences of this are readily apparent. Since, for a V-III flux ratio of 2:1, only an eighth of the incoming atomic flux of As_4 is consumed (as compared with one-fourth for As_2), there is actually a higher As pressure in the vicinity of the substrate than if As_2 were the growth flux. Thus for an arsenic-to-gallium flux ratio of 2:1

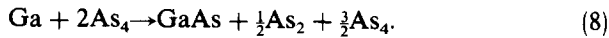
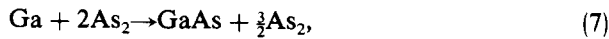


Figure 2 shows the effect of this. The graph shows Eq. (6) for three different As_4 pressures, with the approximation that P_{As_2} is twice P_{As_4} . The real case [Eq. (8)] would be intermediate.

Thus an As_4 flux is at all times significantly more conducive to Ga_3O_3 (or Al_2O_3) formation, and one concludes that As_2 is superior to As_4 for the growth of GaAs and $\text{Ga}_{1-x}\text{Al}_x\text{As}$. Recent work by Künzel and Ploog⁸ confirms this for GaAs .

For the doping of GaAs with magnesium the equation

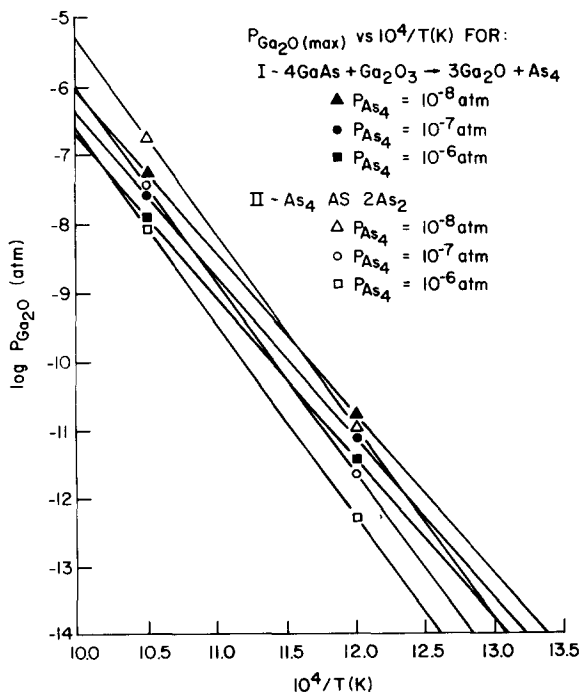


FIG. 2. Maximum allowable Ga_2O pressure vs reciprocal temperature for As_4 over GaAs . Case II treats As_4 as 2As_2 (see text).

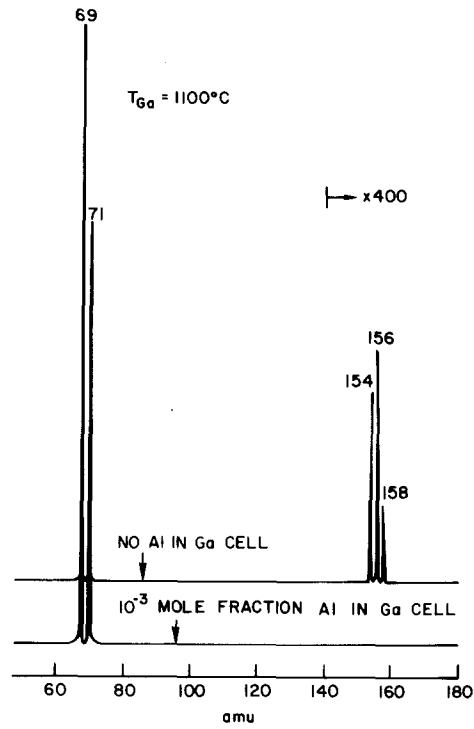
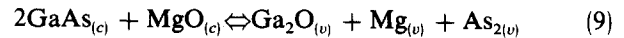


FIG. 3. Intensity vs atomic mass unit (amu) of gallium effusion cell at 1100°C , before and after addition of aluminum. Note $400\times$ scale change for $\text{amu} > 140$. Also, note that Ga_2O (amu 154, 156, and 158) is not detected when Al is added to Ga cell.



applies. Using Cochran and Foster's⁷ data for MgO ,

$$P_{\text{Ga}_2\text{O}_{\text{max}}} = 26.53 - 5.42 \times 10^4/T - \log P_{\text{Mg}} - \log P_{\text{As}_2}. \quad (10)$$

Thus for the hypothetical values of $P_{\text{As}_2} = 10^{-7}$ atm at 600°C and a 10^{15}-cm^{-3} doping of Mg ($P_{\text{Mg}} = 10^{-14}$ atm), the Ga_2O pressure must not exceed 3×10^{-13} atm. Clearly, thermodynamics will favor formation of MgO under virtually any growth conditions, and a low doping efficiency will be observed. The reason Mg dopes $\text{Al}_x\text{Ga}_{1-x}\text{As}$ is that in a probabilistic sense, the Ga_2O will "see" aluminum before it sees magnesium. The Al_2O_3 will be a defect, but it will not interfere with the magnesium dopant.

It is clear that by reducing the volatile oxide pressures in the MBE system, one could alleviate a large number of problems simultaneously. The question is how.

We believe that the gallium effusion cell is the source of most of the volatile oxides. In fact, charging the gallium with oxygen is a purification step for the removal of aluminum and other impurities. This results in the formation of Ga_2O_3 , which in the crucible reacts with gallium to form Ga_2O . In quartz crucibles, there are additional reactions, with gallium and SiO_2 creating Ga_2O , silicon and SiO . The solution we suggest is to add a small amount (0.1%) of aluminum to the gallium in the furnace, with the result that the aluminum ties up the oxygen in relatively less volatile forms. Figure 3 shows the gallium cell's spectrum before and after the addition of aluminum. With aluminum, the Ga_2O (and Al_2O) peaks are indiscernible, whereas, before, the Ga_2O triplet was a major feature of the mass spectrum. Aluminum "con-

tamination" of the gallium arsenide layer is hardly a problem: at about 10^{-4} below the gallium flux, its effect upon the characteristics of the layer are insignificant.

With the rate of arrival of oxides at the surface reduced by several orders of magnitude, we should have the ability to dope gallium arsenide with magnesium. We should also be able to grow better layers of GaAs and $\text{Ga}_{1-x}\text{Al}_x\text{As}$ at higher rates and lower temperatures. Preliminary results support our model. We can state conclusively that we have reduced a major contaminant of the gallium flux to the point where it cannot be measured. This alone is a major accomplishment, and cannot help but improve layer quality.

In conclusion, Ga_2O is shown to be a major contaminant in the gallium growth flux, on the order of 0.1%. Certain conditions, specifically low substrate temperature or high arsenic fluxes, can favor the formation of Ga_2O_3 . The presence of aluminum makes Al_2O_3 formation very probable, with the result that higher substrate temperatures are required. As_2 is shown to be substantially less likely to cause

nonvolatile oxide contamination than As_4 . Drastically lowering the Ga_2O pressure by more than three orders of magnitude by adding a small amount (0.1%) of aluminum to the gallium source will make it possible to grow GaAs and $\text{Ga}_{1-x}\text{Al}_x\text{As}$ at lower temperatures and higher rates. Also, magnesium doping of GaAs at high efficiencies should be possible.

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Fully ion-implanted $p^+ - n$ germanium avalanche photodiodes

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Germanium avalanche photodiodes with a shallow $p^+ - n$ junction have been fabricated using full ion implantation, together with a low temperature (650 °C), single-stage annealing process. This procedure yielded high-performance germanium avalanche photodiodes with a high rate of reproducibility. About 80% of the diodes obtained showed a dark current of 150–250 nA at 0.9 V_B. At a multiplication factor of 10, low excess noise resulted ($F \approx 6.5$ at 1.55 μm and $F = 8$ –9 at 1.3 μm), and deterioration of the response at 500 MHz was limited to 0.5–1 dB.

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There is considerable interest in developing low-noise, low-dark-current, high-speed-response avalanche photodiodes (APD's) for optical-fiber-transmission-system applications in the 1.0–1.6- μm wavelength region. Germanium (Ge) APD's are promising candidates for use as detectors at these wavelengths. Shallow junction $n^+ - p$ Ge APD's were first developed.¹ The $n^+ - p$ structure, however, is not ideal in the 1- μm wavelength region because the ionization rate of holes β is greater than that of electrons α in germanium.^{2,3} At such wavelengths, electron current injected into the avalanche region predominates over hole current in the shallow $n^+ - p$ junction diodes. Therefore the multiplication noise of the $n^+ - p$ Ge APD's has a large value. From the viewpoint of low multiplication noise, the $p^+ - n$ and $n^+ - p$ structures

(hole-injection types) are both considered better, as pointed out by Kaneda *et al.*^{4,5} However, with the $n^+ - n - p$ structure it is difficult to form deep (2–3 μm) n layers with good reproducibility, and response speeds are lower than with the $n^+ - p$

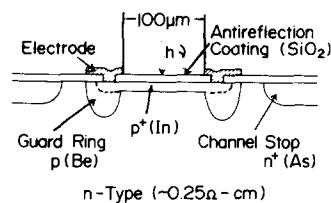


FIG. 1. Cross-sectional view of a $p^+ - n$ Ge APD.