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

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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. Ga_2O is shown to be a major contaminant of 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, a nonvolatile contaminant, on the growth surface and hence in the layer. The presence of aluminum, magnesium, or other highly reactive materials makes oxide incorporation increasingly probable. Drastically lowering the Ga_2O pressure by several orders of magnitude by adding 0.1% aluminum to the gallium effusion cell should allow growth at lower substrate temperatures and higher rates. Magnesium doping of GaAs at unity efficiency is demonstrated as proof of the relevance of the model. Photoluminescence data from the doping experiment are presented.

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I. INTRODUCTION

When growing GaAs and $Ga_{1-x}Al_xAs$ by molecular beam epitaxy, both low substrate temperatures and high growth rates, specifically high arsenic pressures, yield crystals of poor electrical and optical properties.[1,2] The minimum substrate temperature for good-to-high quality GaAs is about 550° C.[1-5] For $Ga_{1-x}Al_xAs$ with $x > 0.1$, the substrate must be maintained at 650° to 700° C.[6] Growth rates are limited to about one micron per hour, with the best V–III flux ratios at about two to one.[1,6] Here we present a volatile oxide model which predicts these observations, as well as others, such as magnesium's low doping efficiency.[4,7,8] The model, combined with experimental results, indicates that Ga_2O poses serious constraints to MBE growth. We show how Ga_2O can be suppressed, and present experimental data where its suppression has allowed magnesium doping of GaAs at unity efficiency.

The volatile oxide model begins by examining the following equilibrium:

$$4GaAs_{(c)} + Ga_2O_{3(c)} \Leftrightarrow 3Ga_2O_{(v)} + 2As_{2(v)} \quad (1)$$

Ga_2O is a readily observed species whose primary source is the gallium oven. As_2 is the growth flux. We will not treat the case of As_4, but assume it to be similar. $GaAs_{(c)}$ represents the crystal surface, and Ga_2O_3 is the nonvolatile oxide that we wish to avoid forming. Using Cho and Arthur's[3] data for the dissociation of GaAs, and Cochran and Foster's[9] data for the disproportionation of Ga_2O, we derive an expression for the maximum allowable pressure of Ga_2O, in atmospheres, in terms of the As_2 pressure and the substrate temperature:

$$\log P_{Ga_2O_{max}} = 17.52 - 2.8 \times 10^4/T - \frac{2}{3}\log P_{As_2}. \quad (2)$$

This equation defines, for a given arsenic pressure and substrate temperature, the Ga_2O pressure that causes the equilibrium to shift from left to right. It is likely that if Ga_2O_3 is formed, it will be incorporated in the lattice as a defect. We propose that this is the mechanism by which high arsenic pressures and low substrate temperatures produce layers of poor electrical and optical properties. For a Ga_2O pressure of 1.5×10^{-10} atmospheres that can be considered as typical for most systems, and an As_2 pressure of 10^{-7} atm (about 1 μm/h), we find that we need a minimum substrate temperature of 600° C to avoid forming Ga_2O_3. In this case, substrate temperatures higher than 600° C and arsenic pressures under 10^{-7} atm act to prevent oxide contamination of the layer. This information is presented numerically as well as graphically in Ref 10.

It must be noted at this point that thermodynamics yields no information concerning rates. The numerical quantities obtained only indicate whether or not the situation is in the process of getting better or worse. Also, thermodynamic data is inherently inexact, especially when dealing with multi-species elements such as arsenic. Thus, only order-of-magnitude comparisons should be made.

For $Al_xGa_{1-x}As$, the reactivity of aluminum leads to the expectation that oxides will be more likely to be incorporated in the layer. Using the equilibrium:

$$6GaAs_{(c)} + Al_2O_{3(c)} \Leftrightarrow 3Ga_2O + 2AlAs + 2As_2 \quad (3)$$

and using Hoch and Hinge's[11] data for AlAs, we derive the equation:

$$\log P_{Ga_2O_{max}} = 13.26 - 2.5 \times 10^4/T - \frac{2}{3}\log P_{As_2}. \quad (4)$$

Thus for a given substrate temperature the allowable Ga_2O pressure is lowered by about an order of magnitude. For our

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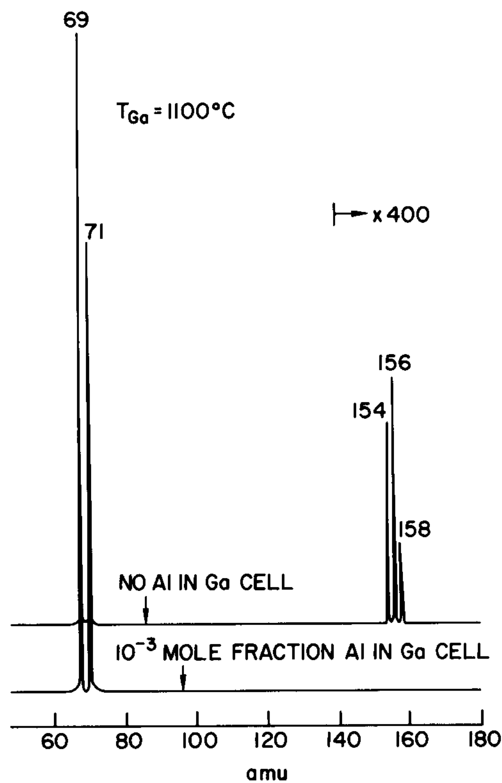

FIG. 1. Intensity vs atomic mass unit (amu) of gallium effusion cell at 1100° C, before and after addition of aluminum. Note 400X scale change for amu >140. Also, note that Ga_2O (amu 154, 156, and 158) is not detected when Al is added to Ga cell.

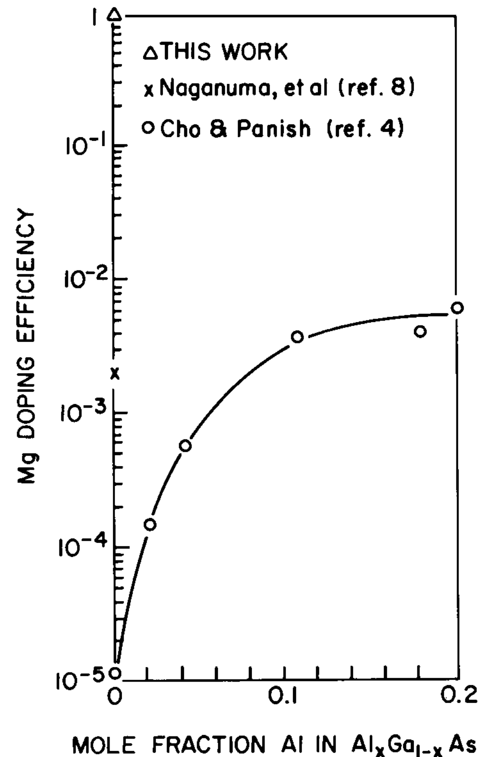

FIG. 2. Previously observed doping efficiencies for magnesium with increasing mole fractions of aluminum in GaAs (o,x). With the addition of aluminum to the gallium cell, the data obtained yields a point of unity efficiency yet an aluminum content indistinguishable from the y-axis (Δ).

system's Ga_2O pressure, the required substrate temperature is about 630° C.

It is clear that by reducing the volatile oxide pressures in the MBE system, one could alleviate a large number of problems simultaneously. 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, first, to use pyrolytic boron nitride crucibles for any cell in which volatile-oxide-producing reactions could occur. Second, for the suppression of Ga_2O, a small amount (0.1%) of aluminum is added to the gallium in the furnace, with the result that the aluminum ties up the oxygen in much less volatile forms. Figure 1 shows the mass spectrum of the gallium effusate before and after the addition of aluminum to the gallium effusion cell. With aluminum, the Ga_2O and Al_2O peaks are indiscernable, whereas before the Ga_2O triplet was a clear feature of the mass spectrum. Aluminum "contamination" 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 insigifnicant. With the rate of arrival of oxides at the surface reduced by several orders of magnitude, some previously observed constraints should be eased. Such is the case with magnesium doping.

II. MAGNESIUM DOPING

For the doping of GaAs with magnesium the following equation applies:

$$2GaAs_{(c)} + MgO_{(c)} \Leftrightarrow Ga_2O_{(v)} + Mg_{(v)} + As_{2(v)}. \quad (5)$$

Using Cochran and Foster's[9] data for MgO leads to the result:

$$\log P_{Ga_2O_{max}} = 26.53 - 5.42 \times 10^4/T - \log P_{Mg} - \log P_{As_2}. \quad (6)$$

Thus for the typical experimental values of $P_{As_4} = 10^{-7}$ atm

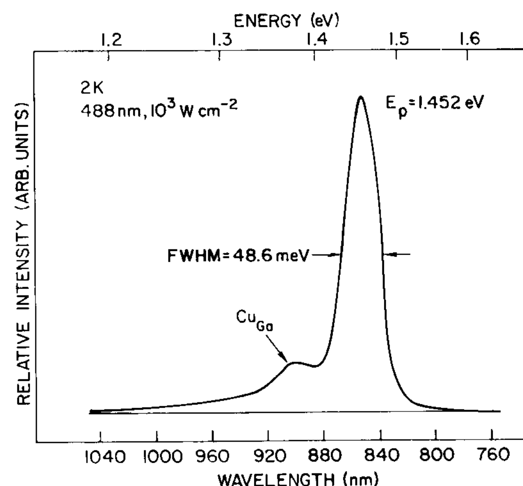

FIG. 3. Photoluminescence intensity vs wavelength for magnesium-doped GaAs layer doped at 1.3×10^{19} cm^{-3}. The position and width of the major peak indicates p-type degeneracy.[12,13]

at 600° C and a 10^{15} cm^{-3} doping of Mg ($P_{Mg} = 10^{-14}$ 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 $Al_xGa_{1-x}As$ is that in a probabalistic sense, the Ga_2O will "see" aluminum before it "sees" magnesium. The Al_2O_3 will be a defect, but more magnesium will remain unoxidized and be able to dope. This effect can be seen in Cho and Panish's data in Fig. 2.[4] Higher efficiencies have been reported,[8] but none approach unity.

The layer that we grew was standard GaAs, except for the Ga_2O supression and our As_2 source. The substrate temperature was held at 550° C, and a 0.9 μ-layer was deposited in three hours. An indium arsenide source was used for As_2 because it was available in high-purity form. Strictly, the resultant indium content of 1% may prove relevant, although we don't consider this likely. Electronically, it proves insignificant, although in thick layers dislocations will result due to a slight lattice mismatch with the GaAs substrate. The magnesium source consists of high-purity magnesium pellets placed in a pyrolytic boron nitride crucible inside a standard effusion furnace. The magnesium flux was set for about 1.8×10^{19} cm^{-3} doping as measured by a quadrupole mass spectrometer located at the substrate's growth position. Comparison with the gallium flux allowed for the efficiency to be calculated once the carrier concentration was determined, since gallium's sticking coefficient is assumed to be unity. Hall measurements gave a free carrier density of 1.3×10^{19} cm^{-3} at room temperature, and a hole mobility of 71 cm^2 V^{-1} s^{-1}. Within experimental error, the conclusions is that all of the magnesium that hit the substrate stuck, and all that stuck doped.

The 2 K photoluminescence spectrum of the magnesium-doped layer appears in Fig. 3. In the range from 800 to 1000 nm, three major radiative recombination transitions are seen. The first or prominent band occurring at about 854 nm cannot be identified with common or well characterized impurity transitions in GaAs. Instead, we attribute it to band-to-band emission between conduction and valence band *tail states* which are expected and known to form in the presence of heavy p-type doping.[12,13] The second appears as a shoulder on the high energy side of the 854 nm peak and marks the abrupt low temperature cutoff of the Fermi level when it lies within the valence band for high acceptor concentrations.[12] The third peak at about 900 nm is identified from doping experiments as copper contamination on gallium sites.[14]

Because of the relative ionization energies of Mg and Zn, 28.4 and 30.7 meV, respectively, it is possible to compare the spectrum with zinc doping data by Cusano[13] and Pankove.[12] Accordingly, the energy of the prominent band-tail transition (1.452 eV) is indicative of a possible Mg doping level of 3–5 $\times 10^{19}$ cm^{-3}. The large transition width of 45–49 meV corresponds to a reported sharp, acceptor-concentration-dependent rise in width only noted above 10^{19} cm^{-3} in Zn-doped GaAs.[12] This suggests a Mg doping level of mid- 10^{19} cm^{-3}.

As shown by photoluminescence and Hall effect measurements, as well as Nomarski microscopy, the magnesium doping experiment produced a degenerately doped GaAs crystal with excellent surface morphology and good electrical and optical characteristics. Mass spectrometry and Hall effect data showed that magnesium incorporated and doped at unity efficiency.

III. CONCLUSIONS

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 growth of $Al_xGa_{1-x}As$ makes Al_2O_3 formation very probable, with the result that higher substrate temperatures are required. Drastically lowering the Ga_2O pressure by several orders of magnitude by adding a small amount (0.1%) of aluminum to the gallium source allows magnesium to dope gallium arsenide at unity efficiency and high concentrations. The lower oxide pressure should also allow the growth of GaAs and $Ga_{1-x}Al_xAs$ at lower substrate temperatures and higher rates. Direct parallels to other dopants and other epitaxial and even nonepitaxial materials may prove useful.

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