Chemical beam epitaxial growth of high-purity GaAs using triethylgallium and arsine

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The growth of high-purity GaAs by chemical beam epitaxy using triethylgallium and arsine is reported. Purity of the epilayer is affected by the cracking efficiency of arsine, V/III ratio, and the substrate temperature. Samples generally show *p*-type conductivity with carbon as the residual impurity. The growth conditions to achieve net carrier concentration below 10^{14} cm^{-3} are identified. The low-temperature photoluminescence spectrum shows well-resolved excitonic structures, an indication of excellent optical quality.

The growth of III-V semiconductor epitaxial layers using metalorganic gas sources in ultrahigh vacuum systems[1-3] has received increasing attention in recent years. With high vacuum little reaction in the gas phase is expected and the growth is mainly determined by the chemical reactions of the source gases on the heated substrate surface. The long mean free path of molecules in high vacuum allows the growth geometry to be determined by the molecular beam distribution which can be easily engineered using a gas diffuser plate. The absence of any memory effect[4] makes possible the preparation of abrupt heterointerfaces under a continuous growth condition using a fast switching gas delivery system. Being able to prepare very high-quality III-V epitaxial heterostructures[5] with abrupt doping profile,[6] chemical beam epitaxy (CBE) has emerged as a powerful growth technology with many advantages, such as superior chemical and lateral uniformity, much reduced growth defect density, precise control of group V species flux densities, fewer high-temperature elements, wide dynamic range of growth rates, semi-infinite source supply without exposing the growth chamber to air, and the availability of high vacuum *in situ* diagnostic tools. For the growth of GaAs in a CBE configuration, it has been reported that the use of triethylgallium (TEG) and arsine (AsH_3) resulted in high-purity GaAs epilayers.[3,7] In the present work, systematic studies of the growth parameters to achieve high-purity GaAs using TEG and arsine by CBE are presented.

The experiments were performed in a Riber CBE 32 system, equipped with a gas manifold employing a growth-chamber/vent configuration and evacuated by a turbomolecular pump (2200 l/s). Triethylgallium was delivered, using hydrogen as carrier gas, through a low-temperature quartz effusion cell maintained at ~80 °C to avoid condensation. This quartz cell was designed with an easily changeable diffuser plate, engineered to achieve excellent lateral uniformity over 3 in. substrate. For the decomposition of arsine, a temperature of 920 °C for the baffled low-pressure cracking cell was adequate for near unity cracking efficiency. However, the relative concentration of the decomposed species has not been determined. Panish and Hamm reported that the majority of the cracked species of a low-pressure cell are arsenic dimers and monomers.[8] The processing gas flow was introduced through an electronic mass flow controller with fast response time. The flow controllers were calibrated with nitrogen without further correction for individual gas employed. With a total flow rate of about 40 cc per minute (sccm) under typical growth conditions, the system pressure was about 3×10^{-5} Torr. Substrate growth temperatures were monitored by an infrared pyrometer calibrated with the melting point of InSb at ~525 °C. A congruent temperature of ~630 °C for GaAs was determined using reflection high-energy electron diffraction (RHEED).

Undoped GaAs epilayers were grown on In-mounted semi-insulating (001) GaAs substrates. All the samples studied showed *p*-type conductivity. The electrical properties were measured from samples of 2–7 μm thickness using the standard van der Pauw technique. The effect of growth temperature on growth rate has previously been determined using the RHEED intensity oscillation technique,[4] revealing the significance of desorption of TEG molecules and their fragmented derivatives from the surface. Under As-stablized condition, the impurity concentration is strongly affected by the growth temperature. Using a V/III ratio of ~2 at a growth rate of ~1.2 μm/h, Fig. 1 shows that the hole density decreases markedly by two orders of magnitude when the substrate temperature changes from 700 to 500 °C. The activation energy is about 2.1 eV for the impurtity incorporation. For the sample grown at 500 °C, the Hall mobility is 518 cm^2/V s with a hole density of 3.6×10^{14} cm^{-3}. The hole mobility as function of hole concentration is plotted in Fig. 2 which compares favorably with the reported 300 K mobility data for *p*-type GaAs.[7]

The *p*-type impurity does not come from the source gases because the same TEG has been used for growing high-purity InGaAs, and the arsine for high mobility GaAs using an elemental Ga source. It has been established using secondary ion mass spectroscopy[3,7] that the dominant *p*-type impurity is carbon. In the CBE growth configuration, there is no gas phase reaction because of low density and low temperature in the beam of metalalkyl source gases. Growth is controlled by the chemical reactions on the heated substrate surface. In the study of Ga- and As-induced RHEED intensity oscillation,[9] it is shown that CBE growth proceeds first with the thermal decomposition of TEG molecules to release free Ga atoms, then the incorporation of As atoms to complete the two-dimensional growth mechanism. The most

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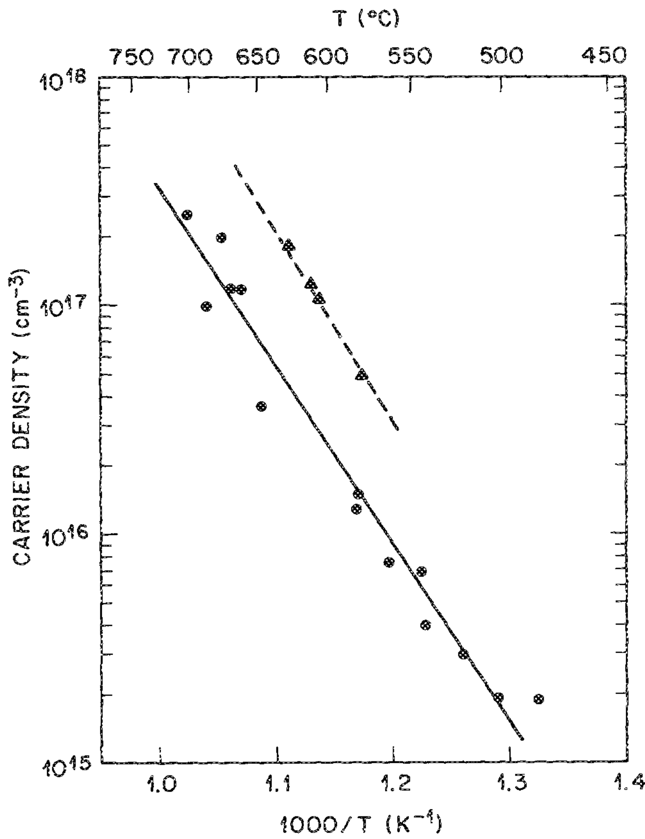

FIG. 1. Arrhenius plot of room-temperature free-hole density as a function of growth temperature. The arsine cracker temperature is 920 °C for solid line and 850 °C for dashed line. The slope gives an activation energy of 2.1 eV.

likely decomposition path is $Ga(C_2H_5)_3 \rightarrow Ga + 3C_2H_4 + 3H$, which is evidenced by the presence of dominant by-product ethylene observed during the growth. Carbon impurity is expected to come from the thermal decomposition of ethylradicals and the carbon incorporation should be less effective at lower growth temperature consistent with the present observations.

The cracking efficiency of arsine and the V/III ratio also affect the purity of CBE grown GaAs. In Fig. 1, when the arsine cracker temperature is lowered to 850 °C while maintaining the same V/III ratio, the hole density increases significantly but the slope gives similar activation energy which is expected if the *p*-type impurity is coming from the decomposition of ethylradicals. Figure 3 shows that at any

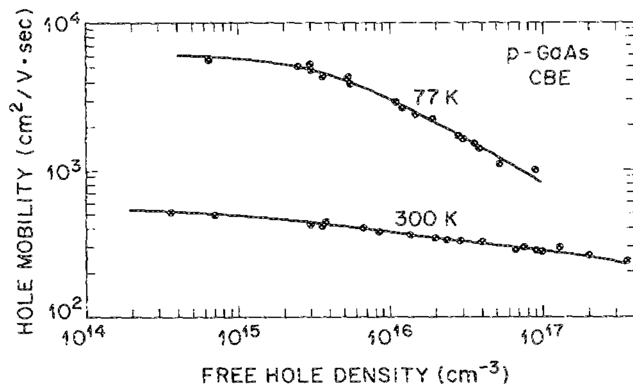

FIG. 2. Hole mobility vs free-hole density ($N_A - N_D$) measured at 300 and 77 K, respectively.

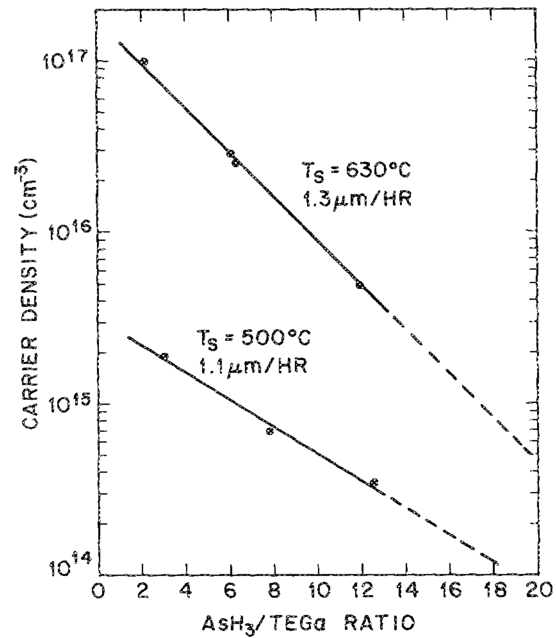

FIG. 3. Room-temperature free-hole density as a function of V/III ratio for samples grown at two different temperatures.

given growth temperature the impurity concentration decreases monotonically with increasing V/III ratio, with stronger dependence at higher growth temperatures in agreement with the observation by Horiguchi *et al.*[3] The maximum V/III ratio in this case is limited to ~15 because of a small total flow rate of the arsine mass flow controller employed. Using a reduced growth rate of 0.6 μm/h at 500 °C and a V/III ratio of 24, a semi-insulating epilayer has

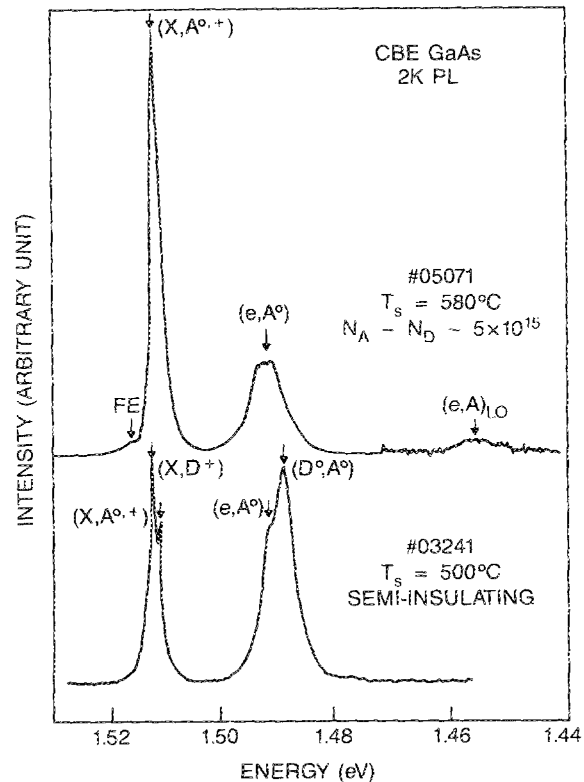

FIG. 4. 2 K photoluminescence spectra for samples grown at (upper) 580 °C and (lower) 500 °C, using V/III ratios of 10 and 24, respectively.

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been obtained. It has been shown that increasing the V/III ratio will lead to conversion from p- to n-type conductivity,[7] characteristic of growth by MOCVD.[10]

The optical quality of these epilayers was evaluated by low-temperature (2 K) photoluminescence (PL) measurements using an Ar^+ laser at 488 nm and a 0.75-m single-pass grating monochromator. Typical results for high-purity samples are illustrated in Fig. 4. The spectrum for the wafer grown at 580 °C with $N_A - N_D \sim 5 \times 10^{15}$ cm^{-3} shows intense acceptor-bound excitonic luminescence (X,A) at 1.512 eV. The free-excition (FE) recombination at 1.5156 eV is clearly resolved. The broad peak at 1.492 eV is due to free electron-to-carbon acceptor transition (e,A^0), and its LO-phonon replica $(e,A^0)_{LO}$ at 1.457 eV is clearly observable. Using an excitation power of 5 W cm^{-2}, a linewidth of 0.5 meV for the (X,A) transition has been measured. For samples with higher hole concentrations grown at 580 °C by reducing the V/III ratio, the (e,A^0) peak intensity increases significantly at the expense of the (X,A) transition; however, the intensity ratio of $(e,A^0)_{LO}$ to (e,A^0) remains relatively unchanged.

For the semi-insulating wafer grown at 500 °C, PL measurement indicates that it is compensated. The peaks at 1.493 and 1.490 eV are identified as band-to-acceptor (e,A^0) and donor-to-acceptor (D^0,A^0) transitions,[11] and the peaks at 1.512 and 1.514 eV as acceptor- and donor-bound excitonic transition. The overall intensity becomes weaker due to the increase of nonradiative recombination traps at lower growth temperatures. Nevertheless, the optical quality is significantly better than that of the wafers grown by molecular beam epitaxy (MBE) using similar growth rate (1 μm/h) and temperature (500 °C). This is most likely due to the fact that rapid surface migration of the TEG molecules[9] plays an important role to achieve stoichiometric growth at low substrate temperature.

In summary, we have shown that a high-purity GaAs epilayer can be grown by CBE using TEG and arsine. The carbon impurity incorporation is affected by the cracking efficiency of arsine, the V/III ratio, and the growth temperature with an activation energy of 2.1 eV. For less carbon impurity, the growth mechanism favors lower growth temperatures which in principle has the advantage of a sharp doping profile. At a low growth temperature (500 °C), the relatively higher surface mobility of TEG molecules compared to Ga atoms may lead to better stoichiometric growth, evidenced by good optical quality from low-temperature PL measurements.

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