

SOLUTION GROWN $\text{Ga}_{1-x}\text{Al}_x\text{As}$ SUPERLATTICE STRUCTURES

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An improved apparatus which employs a solution growth method called isothermal solution mixing (ISM) has been developed for the preparation of one-dimensional superlattice structures of $\text{Ga}_{1-x}\text{Al}_x\text{As}$. Growth by this method occurs when two saturated solutions having different compositions are isothermally mixed together in the presence of a GaAs substrate. Structures have been made which exhibit a one-dimensional periodic variation in composition with a period of 1000 Å and 20 periods thick.

1. Introduction

Recently, a solution growth technique was developed¹⁾ for the growth of $\text{Ga}_{1-x}\text{Al}_x\text{As}$ layers having periodic variations in composition along the growth axis. This technique, called isothermal solution mixing (ISM) growth, was specifically developed to prepare a superlattice structure²⁾ in the $\text{Ga}_{1-x}\text{Al}_x\text{As}$ system. The target structure, already achieved by a vapor growth technique³⁾ in the $\text{GaAs}_{1-x}\text{P}_x$ system, is a crystalline layer having a one-dimensional periodic variation in composition with a period, i.e., the spacing between layers of the same composition, of 100–200 Å. As yet, the predicted transport properties²⁾ of the $\text{GaAs}_{1-x}\text{P}_x$ superlattice structures have not been observed. The reason for this is most likely due to defects generated between the superlattice layers to relieve the strain caused by a considerable mismatch in the $\text{GaAs}_{1-x}\text{P}_x$ system⁴⁾. The $\text{Ga}_{1-x}\text{Al}_x\text{As}$ system has an almost perfect lattice constant match⁵⁾, and it has been shown⁶⁾ to exhibit expected heterojunction transport properties. Therefore, it should be an optimal material for achieving the superlattice properties²⁾.

In a previous report¹⁾, $\text{Ga}_{1-x}\text{Al}_x\text{As}$ superlattice structures with periods of about 2–3 μm and 10 periods thick had been achieved by ISM growth. Unfortunately, the design of the initially reported apparatus did not permit the conditions necessary to achieve the target superlattice structures. In this report we describe an improved apparatus which has yielded superlattice structures with periods as small as 1000 Å, and discuss

the cathodoluminescence and X-ray fluorescence of these layers using an electron beam probe.

2. Experimental

The improved apparatus for the growth of the $\text{Ga}_{1-x}\text{Al}_x\text{As}$ superlattice structure is shown in fig. 1. This figure shows two exploded views of the same apparatus. The entire apparatus is machined from high purity (< 5 ppm residual impurities) high density graphite. Part A is an outer crucible which contains parts B, C, and D when assembled. Part A also prevents rotation of the melt chambers, part D, with respect to substrate holder, part B, and the carbon spacer for melt transfer, part C. A more detailed view of the apparatus is shown by the line drawing in fig. 2. The additional features which can be seen are: (1) a cutaway view of a

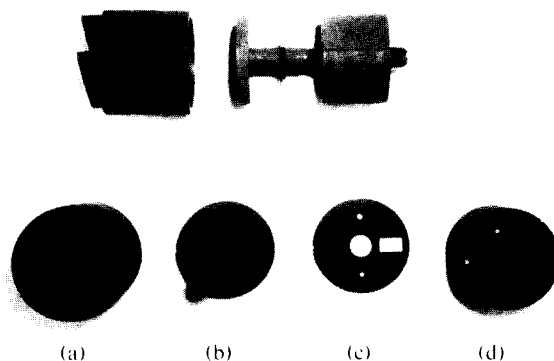


Fig. 1. Apparatus for the ISM growth of thin- $\text{Ga}_{1-x}\text{Al}_x\text{As}$ layers. See text for explanation of A, B, C, and D.

melt chamber with a GaAs source bar (e), (2) a melt chamber (f) with a quartz tube leading to the exterior used to insert a dopant into the melt during growth; and (3) the manner in which the carbon spacer (c) is fixed to the substrate holder (b). In operation the substrate holder and the spacer for melt transfer are rotated from one melt chamber to another via a quartz rod connected from part B to a handle outside of the

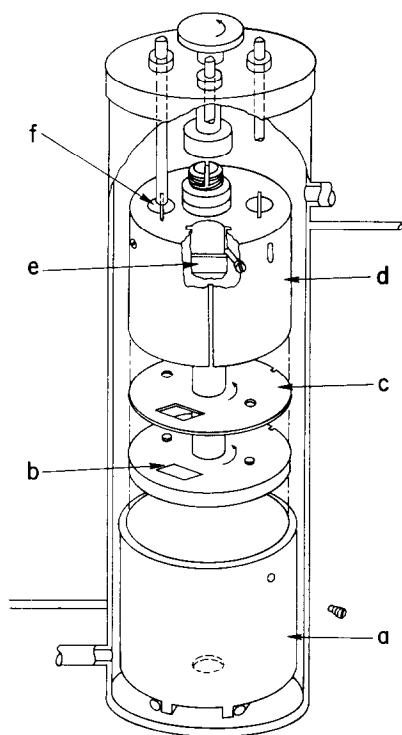


Fig. 2. Line drawing of the apparatus in fig. 1.

quartz containing vessel. The quartz containing vessel is constructed to facilitate vacuum baking, hydrogen back filling, and continuous flushing.

To prepare a growth, a GaAs (100) substrate is lapped to the proper thickness, etched in 1:3:4; HF:HNO₃:H₂O for 30 sec and rinsed in deionized water. The etched wafer is placed into a recess in part B and then part C is placed onto part B thus holding the GaAs wafer in place. Part D is then placed onto the part B and C assembly such that the wafer is located under the venting hole between two of the melt chambers. Next the melt chambers are charged with an etched polycrystalline slab of undoped GaAs. Then, the proper amount of Ga, Al and dopant are loaded

into the chambers. Assembled parts B, C, and D are loaded into part A and the entire assembly placed into the quartz containing vessel. The apparatus is generally vacuum baked at 300 °C for about 30 min to remove any absorbed water from the carbon parts. After back filling with palladium diffused hydrogen and continuous flushing, the apparatus is brought to the crystal growth temperature with a resistance furnace having a uniform temperature profile and controlled to ± 0.1 °C. The temperature is held constant for about one hour to allow each melt to achieve solid-liquid equilibrium. Then, the GaAs wafer is rotated into a position under one of the melt chambers, thus bringing the wafer into contact with one of the melts. At this point crystal growth can be initiated by one of several procedures. In one method the temperature can be lowered at a programmed rate which produces growth by the normal liquid phase epitaxy mode of growth⁷). A modification of this procedure is to rotate the substrate to a position between the melt chambers. This transfers and confines a small volume of melt from the chamber under which the wafer had been positioned. Next, the normal liquid phase epitaxy procedure is used. However, by using small melt volumes, the growth thickness can be controlled to smaller values than those obtained using larger melt volumes for the same cooling rates and total temperature span.

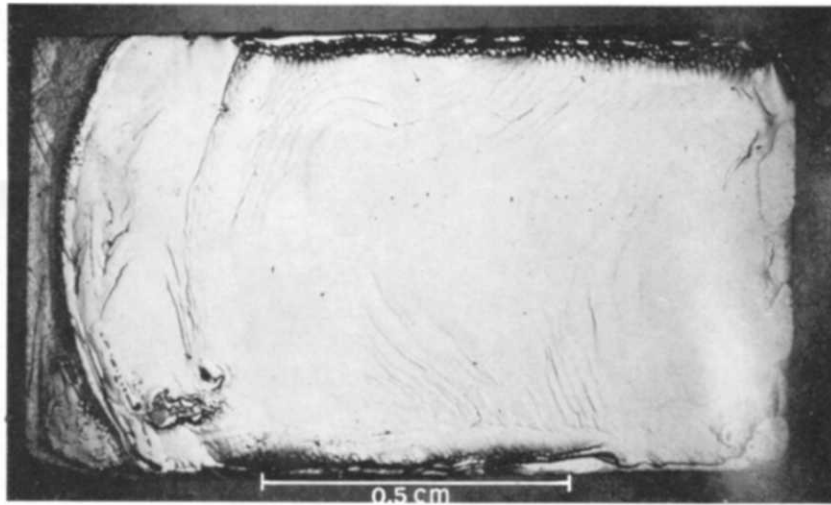
Alternatively, growth can be initiated by maintaining the temperature constant and rotating the substrate back and forth between two melts of different Al concentrations. Growth by this method (ISM) occurs when a small volume of a Ga-rich solution of Ga-Al-As at solid-liquid equilibrium is isothermally mixed with a Ga-Al-As melt at solid-liquid equilibrium having a different composition than the first solution. The mixing of the two solutions results in a new supersaturated solution¹). If a GaAs or $\text{Ga}_{1-x}\text{Al}_x\text{As}$ single crystal solid-liquid interface is located near the solution mixing interface, $\text{Ga}_{1-x}\text{Al}_x\text{As}$ epitaxial layers will deposit. The degree of supersaturation and, hence, the amount of growth, increases with the volume of transferred melt. In the previous apparatus this volume was 0.2 cm³ and it could not be changed easily. However, the transfer volume of the present apparatus is proportional to the thickness of carbon spacer that is used. Furthermore, the spacer design permits smaller transfer volumes than before. For example, a spacer as thin as

0.025 cm, or 0.037 cm³ in volume, can be used without the loss of the solid-liquid interface during transfer. Thus, layers grown with this spacer are about 0.2 times as thick as the layers grown in the previous apparatus with the other growth conditions constant.

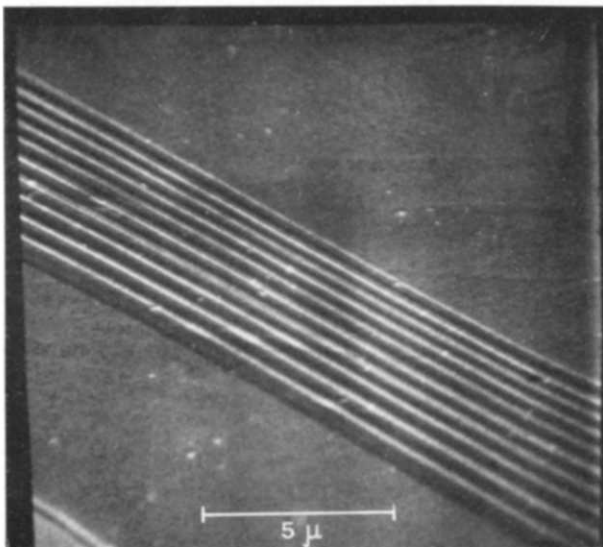
The other parameters which also affect the amount of growth are: melt volume, temperature, composition, and composition difference between the two melts. However, except for temperature, these parameters will not be discussed in this investigation.

3. Results and discussion

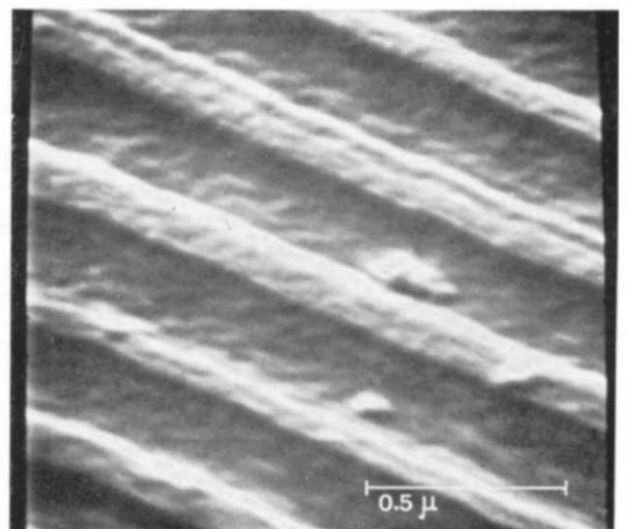
An example of growth by both normal liquid phase epitaxy and ISM is shown in fig. 3. The top of the figure shows a characteristic surface of the growth which occurs during furnace shut down. The layer is fairly smooth with a slight terrace appearance indicating facet growth on the (100) plane. The lower left part of fig. 3 shows a scanning electron photomicrograph of the same layer when cleaved on a (110) plane parallel to



(a)



(b)



(c)

Fig. 3. Ga_{1-x}Al_xAs layer with superlattice region grown by ISM.

the growth direction. The cleaved face has been etched with 1:1:10, $\text{HF}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$, under illumination for 15 sec to reveal the structures. This entire structure was grown in three stages using two melts. Melt 1 was charged with 10 g Ga, 0.010 g Al, 0.002 g Te, and a slab of GaAs. Melt 2 was charged with 10 g Ga, 0.020 g Al, 0.002 g Te, and a slab of GaAs. The first stage of growth started from melt 1 by cooling the furnace from 825°C to 815°C at a rate of $0.1^\circ\text{C}/\text{min}$. This produces a growth $6\ \mu\text{m}$ thick as seen in the area of the photomicrograph (lower left picture of fig. 3) between the line at the lower left corner and the beginning of the superlattice structure.

For the second stage of the growth the furnace was held at $815 \pm 0.05^\circ\text{C}$. Growth was initiated for this stage using the ISM mode by moving the substrate back and forth 20 times between melt 1 and melt 2. The substrate was held for 30 seconds in each melt.

The last melt change brought the substrate into melt 1. The volume of melt transferred by the carbon spacer, part C of fig. 1, was 0.037 ml. The growth of stage 2 is seen as the superlattice region of the photomicrograph (lower left picture of fig. 3). It appears that there are two types of layers in the multilayer growth region. One type appears to etch in the same manner as the material grown in stage 1. The other type appears to etch faster than the first type. It is also seen in the lower right photomicrograph of fig. 3, which is a scanning electron micrograph of the superlattice region taken at a higher magnification, that each type of layer etches homogeneously over the entire superlattice region indicating a high degree of chemical homogeneity within and among the layers. Other data reported below supports this conclusion.

The last stage of growth is done exactly as stage 1. More growth occurs in this stage as a result of furnace

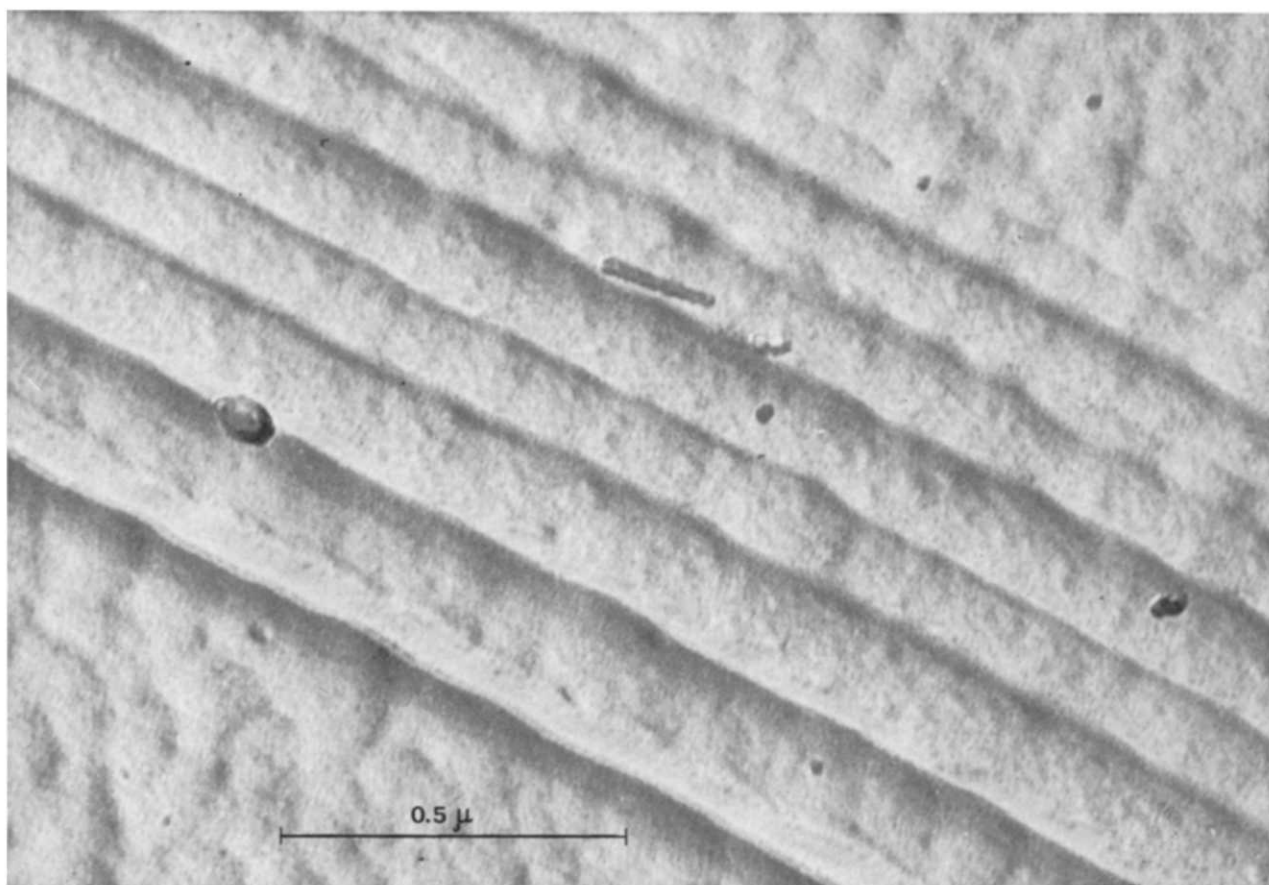


Fig. 4. Electron microscope replica of a superlattice structure with a period of $1000\ \text{\AA}$.

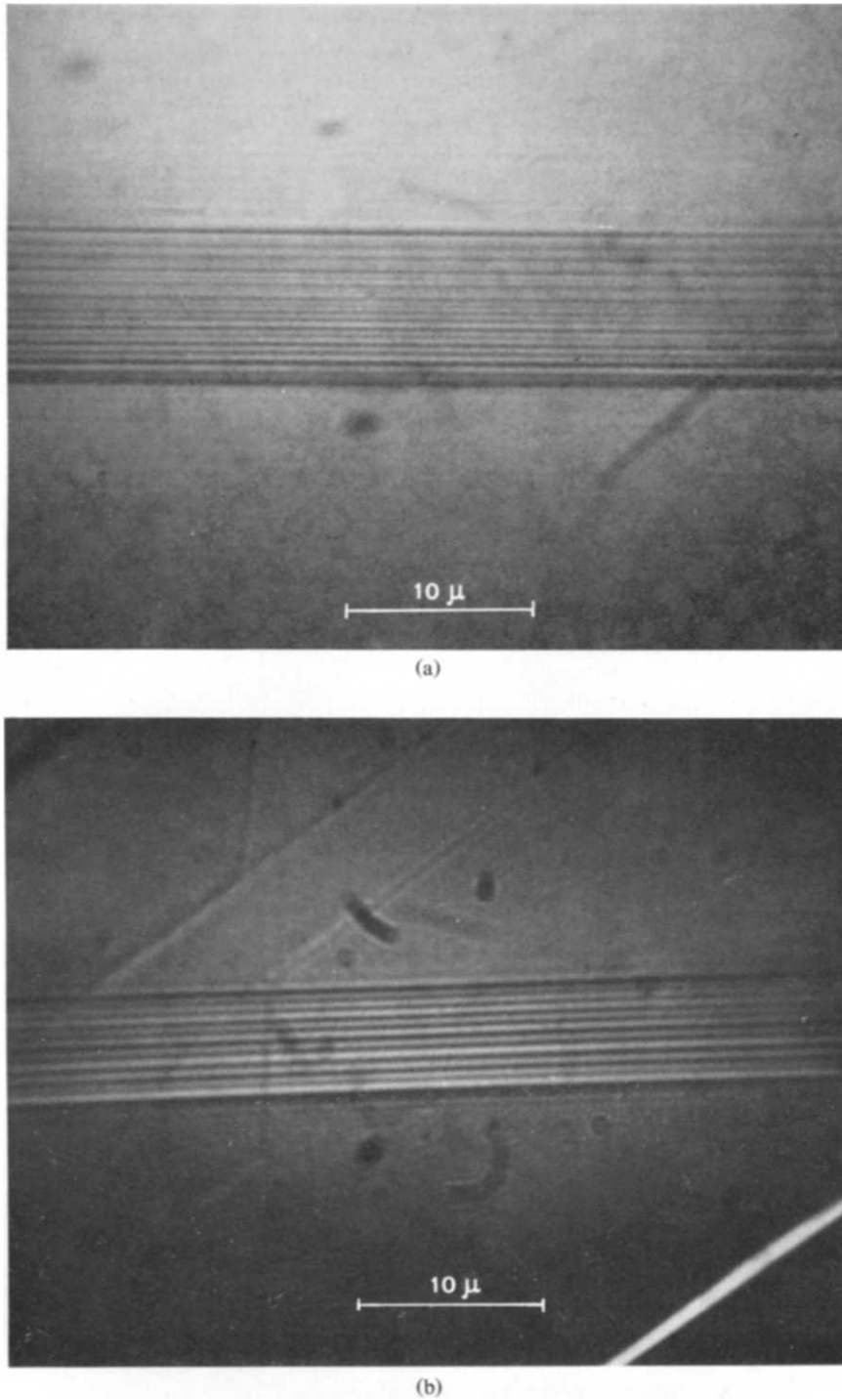


Fig. 5. Photomicrograph comparing the effects of temperature differences between melts on the superlattice structure.

shut down after the 10 °C cool at 0.1 °C/min. Before furnace shut down the substrate is moved between the melt chambers in order to minimize the amount of

growth resulting from furnace shut down.

Superlattice structures with smaller periods can be fabricated by ISM growth at lower temperatures. The

photomicrograph of fig. 4 shows an electron microscope replica of a superlattice structure grown by ISM at 655 °C. The period of this layer is about 1000 Å.

It was found that care must be taken to prevent large temperature differences between melts during ISM growth. The phase contrast photomicrograph of fig. 5 compares the superlattice structures of two growths which differ only in the temperatures between the melt chambers. The top part of fig. 5 shows a superlattice grown melts having a larger temperature difference than the melts used to grow the superlattice structure shown in the bottom part of fig. 5. The larger temperature difference, approximately 1–2 °C, apparently introduces an additional type of layer in addition to those caused by ISM. However, the properties of these types of growths are not understood as yet.

The chemical and optical properties of the superlattice structure have been examined by simultaneously monitoring the cathodoluminescence and X-ray fluorescence generated by an electron beam probe traversing specimens along the growth axis. Again, as for the samples of fig. 3, the growths are cleaved on a (110) plane parallel to the growth axis. These faces are then mounted perpendicular to the electron beam direction. The electron beam probe produces X-ray fluorescence in a hemisphere of material having a diameter of about 1.5 µm.

Some room temperature cathodoluminescence data taken on a superlattice structure is shown in fig. 6. Melt 1 and melt 2 had Al-to-Ga weight ratios of 0.3×10^{-3} and 1.0×10^{-3} respectively. This figure shows two spectral distribution curves. Curve 1 is the cathodoluminescence observed when the probe is positioned on pure GaAs. Curve 2 is the spectra observed when the probe is positioned in the middle of a 10 period superlattice with a period of about 7000 Å. The two separate emission peaks at 1.63 eV and 1.74 eV show that the superlattice region contains two types of layers having distinctly different compositions. Since the intensity of the 1.42 eV peak, due to pure GaAs, increases as the probe is moved away from the middle of the superlattice region it can be concluded that the cathodoluminescence spectra of curve 2 is due to hole electron pairs diffusing away from excitation source and recombining over the entire superlattice region. Thus, curve 2 together with fig. 3 shows that the entire superlattice structure contains layers of material having two

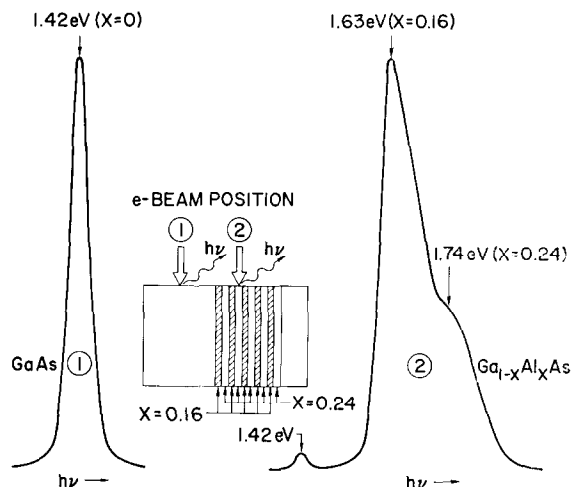


Fig. 6. Cathodoluminescence spectra of a (1) GaAs, and a (2) $\text{Ga}_{1-x}\text{Al}_x\text{As}$ superlattice structure with a 7000 Å period.

different compositional values. The compositional values of each type of layer were calculated to be $\text{Ga}_{0.84}\text{Al}_{0.16}\text{As}$ and $\text{Ga}_{0.76}\text{Al}_{0.24}\text{As}$ using a calibration curve obtained from the cathodoluminescence of homogeneous samples of $\text{Ga}_{1-x}\text{Al}_x\text{As}$. The average composition value determined from the X-ray fluorescence obtained from a probe sampling of several adjacent superlattice layers was found to be $\text{Ga}_{0.8}\text{Al}_{0.2}\text{As}$. As expected, this value lies between the calculated values for each type of layer.

4. Conclusion

An apparatus is described which employs a new solution growth method capable of producing multilayered structures of $\text{Ga}_{1-x}\text{Al}_x\text{As}$ having periodic variations in composition along the growth axis. The individual layers of the multilayer structure have been grown as thin as 500 Å. Room temperature cathodoluminescence and scanning electron microscope studies have shown that structures with periods of about 5000 Å are of good optical quality and that the individual layers are highly uniform in composition. It is anticipated that periods as small as 100 Å can be achieved by this method.

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