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The Growth of a GaAs–GaAlAs Superlattice*

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An ultra high vacuum epitaxy system is described, including special features such as computer control. The system is capable of preparing sophisticated structures requiring a high degree of precise control. GaAlAs films have been grown and evaluated by various techniques; He-ion backscattering and Raman spectroscopy have been shown to be particularly valuable for periodic structures. A structure with a very narrow period has been made, and its transport properties measured and interpreted by the superlattice mechanism.

Introduction

Previously, Esaki and Tsu[1] considered a one-dimensional periodic structure in a monocrystalline semiconductor and analyzed the dynamics of conduction electrons at relatively low density. If such a structure, referred to as a superlattice, has a period shorter than the electron mean free path, nonlinear transport and optical properties would result from the interaction of electron waves with the periodic potential. Of particular interest is the predicted existence of a negative resistance resulting from the decrease of velocities when electrons in momentum space move toward the boundary of the minizone created by the superlattice potential. Since the predicted properties depend critically on the period and the amplitude of the periodic potential, it was proposed to introduce such a potential by a periodic variation of the alloy composition during epitaxial growth of III-V compound semiconductors, rather than to rely on layered materials naturally in existence such as SiC.[2] The success of forming the structure clearly requires high-quality epitaxy with precise control of the periodicity and extreme smoothness in growth interfaces.

We have employed the process of vacuum evaporation using GaAs and its alloys, $Ga_{1-x}Al_xAs$, for making the superlattice structure. The evaporation process was selected because of the relative ease in controlling thickness and because of the possibility of using low substrate temperatures, thereby reducing the effect of interdiffusion. The materials were chosen because of the excellent matching of both lattice and force constants[3,4] which should minimize crystal imperfections. The use of a "three-temperature" vacuum evaporation technique to grow III-V compound semiconductors was originated by Gunther.[5] His technique depends on an excess flux of the group V elements to compensate for their high volatility at growth temperatures. Subsequently, Davey and Pankey[6] succeeded in growing epitaxial GaAs films using a modified technique. The kinetics of the reaction mechanism was studied by Arthur,[7] who showed that the sticking coefficient of Ga on a GaAs surface is unity and that of As_2 increases to unity for a Ga covered surface. Arthur and LePore[8] successfully grew epitaxial films of both GaAs and GaP. Using the same technique, Cho, Panish, and Hayashi[9] have obtained smooth films of GaAs, GaP, and GaAlAs, and recently Cho[10] demonstrated the feasibility of forming layered structures of GaAlAs. In this paper, we describe a computer-controlled, ultrahigh vacuum evaporation system specifically designed for preparing superlattice structures. We also discuss various measurements for their evaluation and present preliminary transport properties.

I. Epitaxy System

Our ultrahigh vacuum evaporation system has a 24-in.-diam pumping module consisting of 24 magnetic ion pumps mounted on its periphery, each having a pumping capability of 25 liters/sec, together with a 45 000 liters/sec titanium sublimation pump with a liquid-nitrogen-filled shroud. This module is separated by a 14-in.-diam poppet valve of $2\frac{1}{2}$ inch travel from a working chamber where the vacuum deposition is performed. A quadrupole mass spectrum analyzer (modified UTI 100B model) and a scanning high energy electron diffraction (SHEED) system (Vacuum Generators, England) are attached to the chamber. The electron gun and analyzer chambers of the SHEED system have additional auxiliary ion pumps. The whole system is bakable at 250°C. After overnight baking, the pressure in the chamber, with all the component parts installed as described in the following, falls in the range of 10^{-10} Torr prior to evaporation.

Figure 1 shows, schematically, the whole assembly including the data flow for computer control. Six effusion ovens were installed, which are surrounded by a liquid-

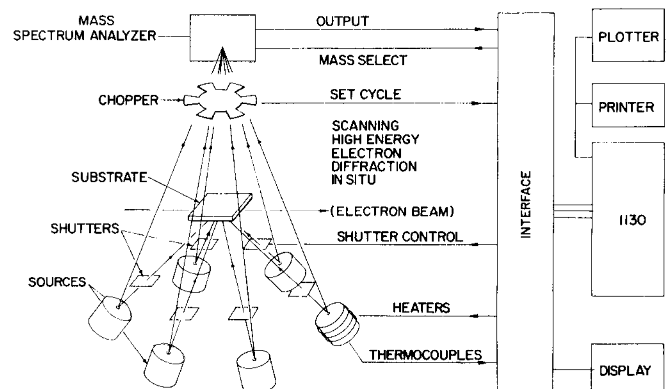

FIGURE 1. A schematic diagram of the evaporation system, including the computer control through the interface.

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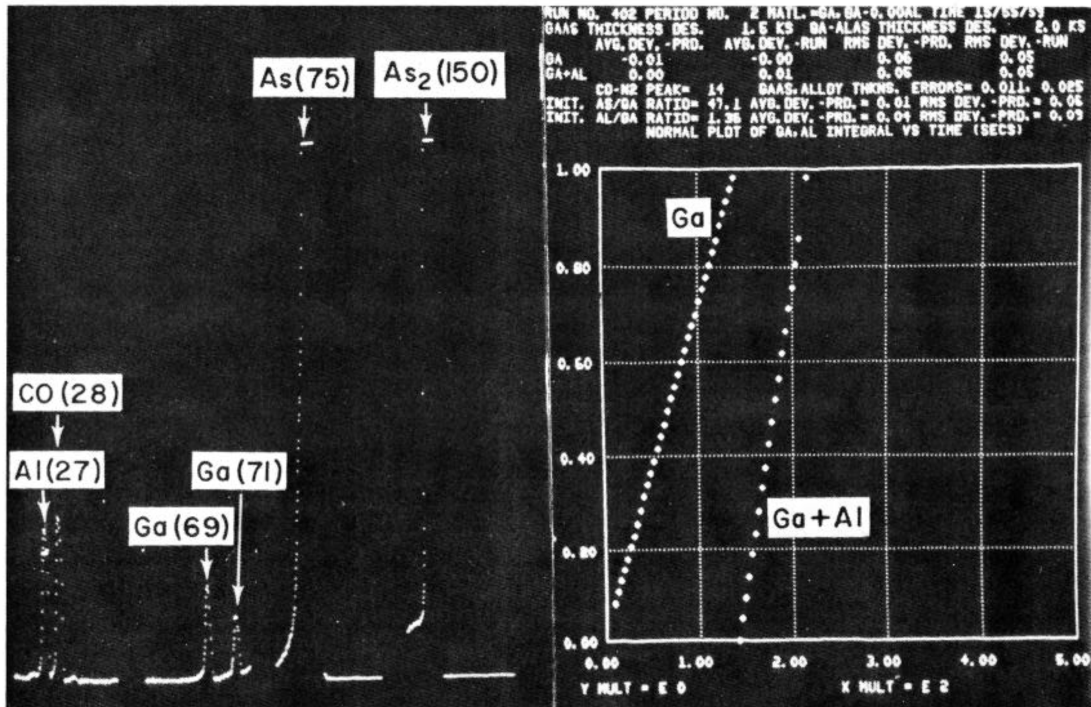

FIGURE 2. Display from the mass spectrum analyzer of the vapor species of interest during the growth of GaAlAs. On the right is shown the time-integrated values of Ga and Ga+Al vs time to demonstrate the control for growing a periodic structure.

nitrogen shroud. Each temperature-controlled oven has its own shutter, operated pneumatically within one-tenth of a second. All atomic or molecular beams from the ovens are collimated toward the substrate holder and the analyzer by oval-shaped openings on the lid of the nitrogen shroud. The analyzer is located in a separate chamber above the substrate, allowing the various vapor species to be monitored. The distances from the ovens to the substrate and to the analyzer are 3 and 9 in., respectively. The incident angles of all beams impinging on the substrate are designed to be about 15°. In the present experiment, five ovens are used, containing GaAs, primarily as a source of As_2; Ga and Al, for determining the growth rate and alloy composition; and Sn or Ge for controlling the impurity concentration. The substrate holder is attached to a universal manipulator for precise positioning. The chopper is used for setting the time cycle in computer control, to be discussed in Sec. II. The temperatures of the ovens and the substrate are measured with 3% versus 25% rhenium–tungsten thermocouples.

The substrates were single crystalline GaAs wafers of (100) orientation, having dimensions of $\frac{1}{2}\times\frac{1}{2}$ in. and a thickness of 20 mils. Both semi-insulating and conducting (electron concentration $\sim 10^{17}$ cm^{-3}) substrates have been used. The wafers were chemically polished and, just prior to loading into the system, etched in a dilute solution of sodium hypochlorite. After evacuation to 10^{-9} Torr, the substrate was heated at 600–620°C for 1 h and then lowered to 500–600°C for deposition, 580°C being a typical temperature. The oven temperatures can be varied over wide ranges to give growth rates of 0.1–10 Å/sec, and alloys up to high Al compositions. Typically, the Ga oven was heated to 1000°C to produce an arrival rate at the substrate of $10^{14}/cm^2$ sec for our geometry; the temperatures of the GaAs and Al ovens were then adjusted to give a ratio of As_2 to Ga equal to about 10 and an Al composition in the range of 30%–50%. The various effusion and consumption rates involved can be estimated quite accurately from the known data of equilibrium vapor pressures.[11,12]

II. Computer Control

The ability of the evaporation system just described to provide accurately controlled epitaxial structures rests ultimately on the stability of the mass analyzer. But the capability of preparing complex structures using various control strategies is inherent in the use of a general-purpose computer as the analytic element of the control system. This can best be illustrated by discussing the operation of the system under a typical control process.

In the growth of a periodic structure, as stated earlier, it is important to control both the thickness and the alloy composition. The latter requirement implies that the relative effusion rates for at least two sources (Ga and Al in the present case) be controlled, which can be most easily achieved by maintaining both rates constant. This can be done by means of a double loop control system. The interface shown in Fig. 1 includes analog temperature controllers for the source ovens, the set points of which can be adjusted by the computer, based on actual rates sensed by the mass analyzer. Such a dual system has the advantages of facilitating manual operation for testing and preparation, and achieving effective rate control regardless of any changing conditions that may occur in the source ovens.

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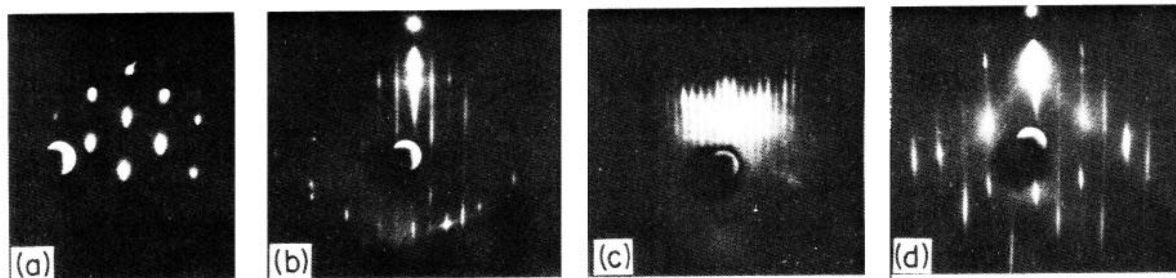

FIGURE 3. 20 kV HEED Patterns in the growth of a GaAs–GaAlAs superlattice on (100) oriented substrates. (a) Substrate prior to deposition, [110] azimuth; (b)–(d), $C(2\times8)$ structure after completion of deposition: (b) [110] azimuth; (c) $[1\bar{1}0]$ azimuth; (d) [100] azimuth.

To grow a superlattice, two programs are used in succession, one for calibration and entry of parameters, and the other for controlling the operation. The first program repeatedly scans the regions of interest in the mass spectrum and displays on a CRT the average results as shown in Fig. 2. It also requests desired thickness, number of periods, etc. The chopper is then started and the main program is loaded. The chopper sets the timing for the whole control program, since it is important to distinguish between data taken with the chopper open and closed. Each opening or closing (period ~2 sec) thus produces an interrupt in the computer and initiates data acquisition; now only the mass peaks of interest are scanned, e.g., ^{27}Al, ^{69}Ga and $^{150}As_2$. Prior to deposition, the peak heights which are to be maintained during the growth are established by repeated scans. GaAs is grown by opening both the GaAs and Ga shutters. The time-integrated value of the Ga peak height is displayed on the CRT versus time as shown on the right of Fig. 2. As soon as it reaches the desired value, normalized to 1.00 on the display, the Al shutter is opened and the Ga shutter is either left open or closed, depending on the alloy composition desired. In the former case, the sum of both the Ga and the Al values are then integrated and displayed, as shown. The cycle repeats itself until a prescribed number of periods is completed. The information printed on top of the figure describes the objectives and progress of the operation, including average deviations and fluctuations from ideal control. During each chopper cycle, in addition to integration and plotting, the deviations of peak heights from their initial values are registered and used to generate source temperature corrections through a standard control algorithm. The program provides an initial underlay of GaAs, a specified number of periods of superlattice, and a final overlay of GaAs.

III. In Situ Surface Evaluation

The SHEED system, as indicated in Fig. 1, is attached to the evaporation system for *in situ* surface studies to ensure that the growth meets the stringent requirements of smoothness in a superlattice. It is basically a high energy electron diffraction (HEED) system with the added feature that the entirety of diffracted beams are magnetically deflected in a raster scan about a small central aperture. Electrons passing through the aperture are detected by a multiplier whose output is superimposed on a corresponding raster scan and displayed on an X–Y recorder. The finished recording has the appearance of a pseudo-three-dimensional plot of the diffraction pattern. SHEED has basically a twofold advantage over conventional HEED: precise quantitative measurement of diffracted beam intensities and elimination by means of the energy filter of a possibly confusing background of inelastically scattered electrons. We have made use of the scanning capability to determine precise spacing intervals of surface structure. Furthermore, we have observed periodic variations, during superlattice growth, of the diffraction intensity due to the difference in the atomic scattering amplitudes for Ga and Al. The system can also be used in the conventional HEED mode, as it incorporates a phosphor screen for viewing. The HEED patterns contain a great deal of qualitative information sufficient for the purpose of the present work.

For *in situ* observation during growth, the geometry requires the reflection mode of HEED operation with glancing angles of 1° or less. Figure 3 shows diffraction patterns under typical experimental conditions as mentioned earlier. The spotty pattern in Fig. 3(a), taken prior to deposition, is attributed to transmission diffraction through surface irregularities. The streaking patterns in Figs. 3(b)–3(d), each for a different azimuth as indicated, were taken when the growth of the superlattice was completed. Actually, the patterns begin to streak already after growth of only a few hundred Å. The conversion to streaking patterns is a consequence of the smoothing of the surface, which appears to the grazing electron beam as a two-dimensional lattice, thus relaxing the Bragg condition in the direction normal to the surface. The observation of the streaking patterns implies that the surface roughness has an rms value of less than 10 Å.

As also can be seen in Figs. 3(b)–3(d), intermediary streaks appear because of the reconstruction of the surface into a periodic, two-dimensional surface structure with a cell spacing larger than that of the bulk material. Depending on the growth conditions, Cho[18] and co-workers[9] have found a great number of surface structures on GaAs. Figures 3(b) and 3(c) show the $C(2\times8)$ structure on the ⟨110⟩ azimuths which was reported previously.[18] However, we have observed a new surface structure when the As_2/Ga ratio is increased

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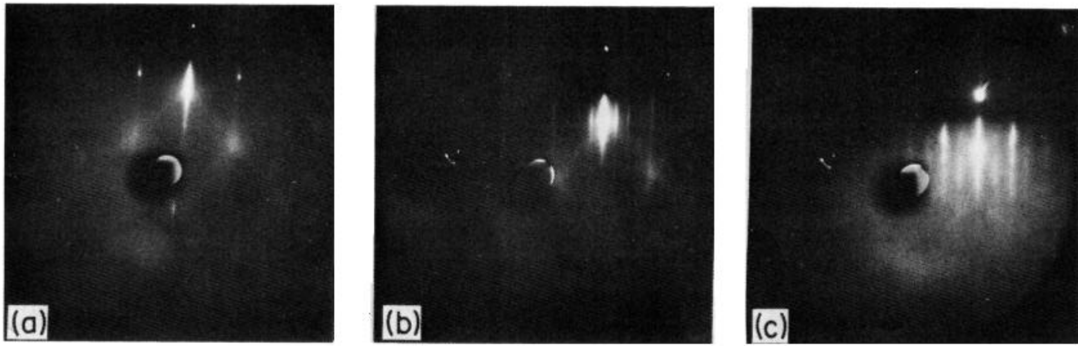

FIGURE 4. 20 kV HEED patterns to show reconstructed surface structures on (100) GaAs. (a) $C(2\times8)$ structure, [100] azimuth; (b) (4×4) structure, [100] azimuth; (c) (2×2) structure, $[1\bar{1}0]$ azimuth.

and/or the substrate temperature is lowered. This structure assumes a (4×4) symmetry in the $\langle 100\rangle$ azimuths where under previous growth conditions no apparent extreneous structure existed, as shown in Fig. 4(a). Figure 4(b) shows this new structure for the [100] azimuth, the other orthogonal [010] azimuth exhibiting the same pattern. Simultaneously, the $\langle 110\rangle$ azimuthal structure is changed from the $C(2\times8)$ structure of Figs. 3(b)–3(c) to a (2×2) structure, the $[1\bar{1}0]$ azimuth being shown in Fig. 4(c). The other [110] azimuth remains unchanged and identical to Fig. 3(b). The introduction of Al makes the situation even more complicated; for example, the typical GaAs $C(2\times8)$ structure on the $\langle 110\rangle$ azimuths switches to a (3×1) structure soon after the Al beam impinges on the substrate with the Ga beam turned off. Our present concern for preparing a superlattice is to achieve atomically smooth growth; a detailed mapping of the various surface structures and their dependence on the experimental condition is clearly beyond the scope of this paper.

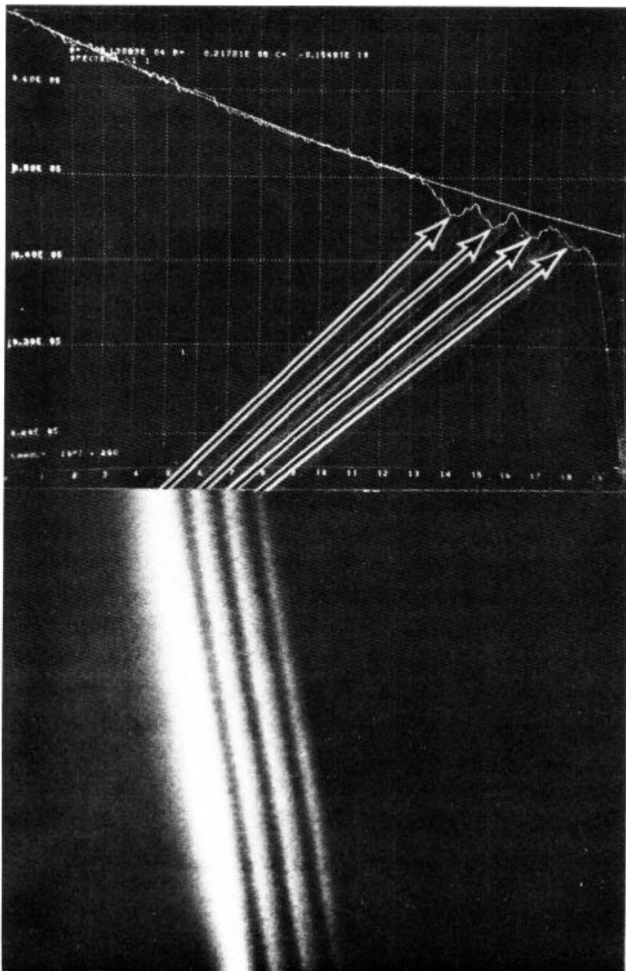

FIGURE 5. Evaluation of a GaAs–$Ga_{0.7}Al_{0.3}As$ periodic structure having 4 periods with each period 800 Å thick. The upper photograph is a profile from He-ion backscattering and the lower photograph is an electron micrograph of the cross section with a magnification of 52500.

IV. Grown Films

Extensive Van der Pauw measurements were made as an initial evaluation of the epitaxial GaAs. The films are all n-type, having a carrier concentration varying from 10^{16} cm^{-3} to 5×10^{18} cm^{-3} with corresponding mobilities of 4000 cm^2/V sec to 1500 cm^2/V sec at room temperature. While these mobilities are considered satisfactory, they are still lower than the better values reported for liquid-phase epitaxial (LPE) GaAs.[14] On adding Al, both the carrier concentration and the mobility decrease, and the films become high-resistivity when the Al composition is beyond 20%. Cathodoluminescence measurements at 4.2 K exhibit a near-gap peak at 1.52 eV for GaAs with an intensity, in general, about a factor of 2–5 lower than that of LPE crystals. Near-gap emission was also observed at 4.2 K for $Ga_{1-x}Al_xAs$ with x up to 0.5.[15,16] But the results are not reproducible for various growths without apparent change in experimental conditions. The Al composition has been determined by electron microprobe analysis, ^{4}He-ion backscattering, and Raman spectroscopy. The results from these various techniques are in good agreement and their consistency for different regions of the substrate indicates adequate uniformity.

The techniques of ^{4}He-ion backscattering and Raman spectroscopy are of particular interest because of their usefulness in evaluating the periodic structures. For the purpose of illustration, a structure of GaAs–$Ga_{0.7}Al_{0.3}As$ having four periods with each period of thickness 800 Å is prepared and examined by these techniques. The upper photograph in Fig. 5 shows the energy distribution of backscattered He ions. The expected oscillatory behavior is observed, providing a profile of Ga composi-

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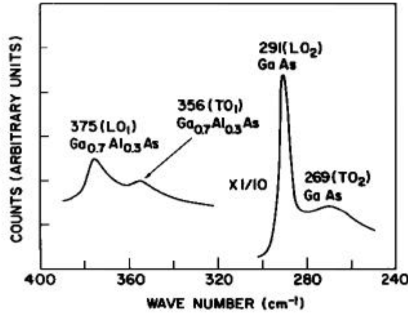

FIGURE 6. Raman spectrum of the same periodic structure shown in the previous figure.

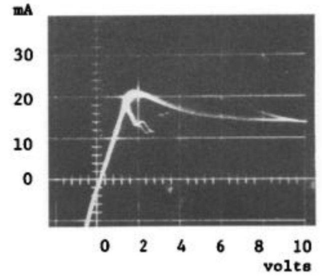

FIGURE 7. Current–voltage characteristic at room temperature of a 70-Å-period, GaAs–$Ga_{0.5}Al_{0.5}As$ superlattice.

tion in the structure.[17] Each dip in the curve represents a deficiency of Ga atoms, and thus corresponds to an alloy region. Knowing the energies of the primary ions (2.5 MeV) and the scattered ones, and the rate of energy loss, both the composition and the period are determined and found to be as intended. The lower photograph in the figure is an electron micrograph of the cleaved and etched cross section of the same growth. The bright stripes in this case represent GaAlAs and are a consequence of the slower etching rate. The Raman spectrum taken on the same growth with a 5145-Å Ar laser is shown in Fig. 6, where two sets of phonon peaks are clearly seen. Using recent results of mode frequencies versus composition in GaAlAs,[18] the two regions can be identified as pure GaAs and $Ga_{0.7}Al_{0.3}As$. It is significant to note that despite such small dimensions, two distinct regions exist in the structure. In fact, the distinction persists to even smaller dimensions well below 100 Å, as in the superlattice to be discussed below. In this regime, the Raman spectroscopy at present seems to be the only technique available for evaluation.

Superlattice structures made for transport measurements typically have 100 periods with each period consisting of a GaAs layer of $\sim$60 Å thick and a $Ga_{0.5}Al_{0.5}As$ layer of $\sim$10 Å thick. Substrates of n-type GaAs with a carrier concentration of 10^{17} cm^{-3} were used. The superlattice structure was grown between two similarly doped GaAs layers of 2000 Å each; the underlay for smoothing the growth as discussed earlier and the overlay for facilitating the formation of an ohmic contact. Mesa-type devices were etched with an active area of the order of 10^{-6} cm^{-2}. The current–voltage characteristic taken at room temperature with a 60 cycle curve tracer is shown in Fig. 7. A negative resistance can be seen to exist beyond 2 V. This characteristic is symmetrical with respect to voltage polarity and persists to 10 nsec in pulsed measurements. The analysis of this observation in the framework of the superlattice is discussed elsewhere.[19] In order to explain briefly the nature of the interpretation, we show in Fig. 8 a calculation of energy–wave number relationship in the first minizone along the direction of the superlattice. The two curves are calculated for a Kronig–Penny δ-function potential, as depicted in the figure, and for two sets of parameters approximating the experimental situation. It is seen that the first allowed band is not much larger than kT whereas the first energy gap is several kT. The conduction electrons, about 10^{16} cm^{-3}, are thus virtually confined in the band. In this case, the theoretical threshold condition for a negative resistance is given by $eF\tau d/h \sim 1$, where F is the field and τ is the scattering time, assumed constant in the treatment.[1] This quantity turns out to be $\sim$2 in our experiment, using $F = 2\times10^4$ V/cm and $\tau \cong 10^{-13}$ sec as estimated from the mobility value. The agreement within a factor of 2 seems to support the interpretation in terms of a superlattice electron dispersion mechanism.

V. Summary

We have described an ultrahigh vacuum epitaxy system with the following features: six sources for multiple evaporation, mass analyzer for spectroscopic monitoring, SHEED for *in situ* studies, and computer for precise control. Although it is designed and is currently used specifically for the growth of GaAs–GaAlAs superlattice, the versatility and capability of the system promise its use in the preparation of a variety of structures, with a great number of materials, that require a high degree of sophistication. GaAlAs films have been grown at rates ranging from 0.1 to

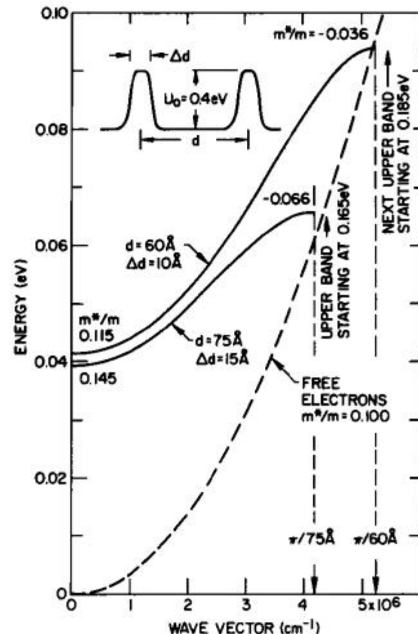

FIGURE 8. E vs k in the first allowed band for two superlattice structures (solid curves) and for the free electron case (dashed curves). The potential profile is shown in the upper left-hand corner. The values of the effective mass at $k=0$ and $k=\pi/d$ are indicated on each curve.

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10 Å/sec and with an Al composition up to 80%. The grown films have been evaluated by several techniques including He-ion backscattering and Raman spectroscopy, both of which are shown to be particularly useful for periodic structures. The superlattice structure made with GaAs–$Ga_{0.5}Al_{0.5}As$ having a period of 70 Å has been measured electrically; a negative resistance has been observed and interpreted satisfactorily by the mechanism of electron-superlattice interactions.

Acknowledgments

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