Long-Range Order in $Al_xGa_{1-x}As$

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We report the first observation of long-range order in a semiconductor III-V ternary alloy. $Al_xGa_{1-x}As$ thin crystals grown by metal-organic chemical vapor deposition or molecular-beam epitaxy have Ga atoms preferentially occupying the 0,0,0 and $\frac{1}{2},\frac{1}{2},0$ sites and Al atoms the $\frac{1}{2},0,\frac{1}{2}$ and $0,\frac{1}{2},\frac{1}{2}$ sites in each unit cell. Our results indicate that this ordered structure is the equilibrium state of $Al_xGa_{1-x}As$.

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The growth of monolayer AlAs-GaAs superlattices by alternate molecular-beam depositions of monolayers of AlAs and GaAs has been successfully demonstrated.[1] Nevertheless, at molecular-beam-epitaxy (MBE) growth temperatures ($\sim 600\,^{\circ}C$) the AlAs and GaAs layers are expected to be fully miscible.[2,3] The clear separation of these layers is thus surprising and the pinning of the AlAs layers by impurities incorporated during the growth has been suggested.[4] In this Letter we report electron-microscope studies of uniform $Al_xGa_{1-x}As$ films grown epitaxially on (110)- or (100)-oriented GaAs substrates. We find that a periodic compositional modulation on an atomic scale (i.e., a long-range order) not imposed artificially during the growth process is present in $Al_xGa_{1-x}As$ films. This is the first long-range order ever observed in a semiconductor III-V ternary alloy. Our observations strongly suggest that this ordered structure, which takes the form of a monolayer superlattice, is the equilibrium state of $Al_xGa_{1-x}As$ at temperatures below about 800 °C. This would imply that monolayer superlattices grown on (110)- or (100)-oriented substrates are thermodynamically stable.

We have examined a large matrix of $Al_xGa_{1-x}As$ films which were grown over a range of substrate temperatures from 600 to 800 °C and compositions from $x=0.25$ to 0.75 using the metal-organic chemical vapor deposition (MOCVD) technique. In this technique the $Al_xGa_{1-x}As$ films were grown through the copyrolysis of $Ga(CH_3)_3$, $Al(CH_3)_3$, and AsH_3 on GaAs substrates. All the $Al_xGa_{1-x}As$ films, nominally undoped, were 0.3–0.5 μm thick grown on a 0.1-μm GaAs buffer layer at a rate of 3 μm/h. The background impurity content of the films was found to be less than $10^{17}/cm^3$.

In the $Al_xGa_{1-x}As$ alloy system the column-III (Ga,Al) atoms and the column-V (As) atoms are placed in two separate fcc lattices displaced from each other by one-quarter of a body diagonal. The change in lattice constant from GaAs to AlAs is very small (about 0.12% at room temperature). On the basis of structure-factor considerations, if the Ga and Al atoms are distributed randomly amongst the column-III sites, then those x-ray or electron reflections with mixed *hkl* indices (e.g., 100, 110, 210, 211, . . . , etc.) are forbidden. However, from crystals grown at a temperature specific to a given composition and substrate orientation, as tabulated in Table I, we have observed a set of forbidden reflections (e.g., 001, $\bar{1}10$, $\bar{1}12$, 110, 130, . . . , etc.) due to an ordered structure. The intensities of these superstructure reflections observed from $Al_{0.75}Ga_{0.25}As$ grown on (110) GaAs at 700 °C, as shown in Figs. 1(a) and 1(b), are the strongest among all the samples studied. The patterns in Figs. 1(a) and 1(b) were obtained with an incident electron beam (200 keV in energy) parallel and perpendicular to the [110] growth axis, respectively. In the cross-sectional diffraction pattern [Fig. 1(b)], there are streaks parallel to the growth axis and superimposed on the superstructure reflections.

TABLE I. Intensities of superstructure reflections observed from $Al_xGa_{1-x}As$ thin crystals grown on GaAs by MOCVD.

Substrate orientation	Al content (x)	Growth temperature 600 °C	650 °C	700 °C	800 °C
(110)	0.25	. . .	weak	. . .	. . .
	0.50	weak	weak	medium	weak
	0.75	weak	medium	strong	weak
(100)	0.25	. . .	. . .	weak	. . .
	0.50	. . .	. . .	. . .	. . .
	0.75	. . .	. . .	. . .	weak

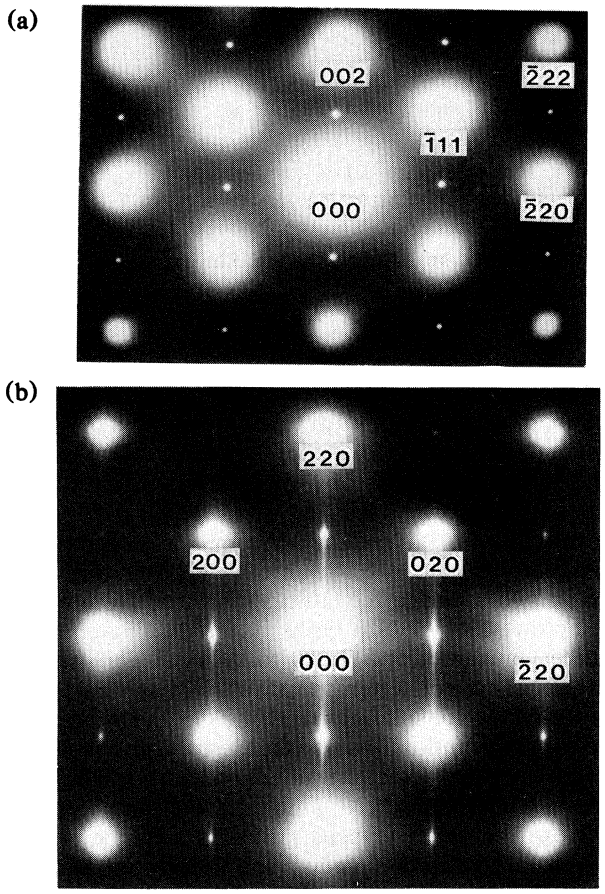

FIG. 1. (a) (110) diffraction pattern and (b) (001) pattern from a $Al_{0.75}Ga_{0.25}As$ film grown on a (110) GaAs substrate by MOCVD at 700 °C.

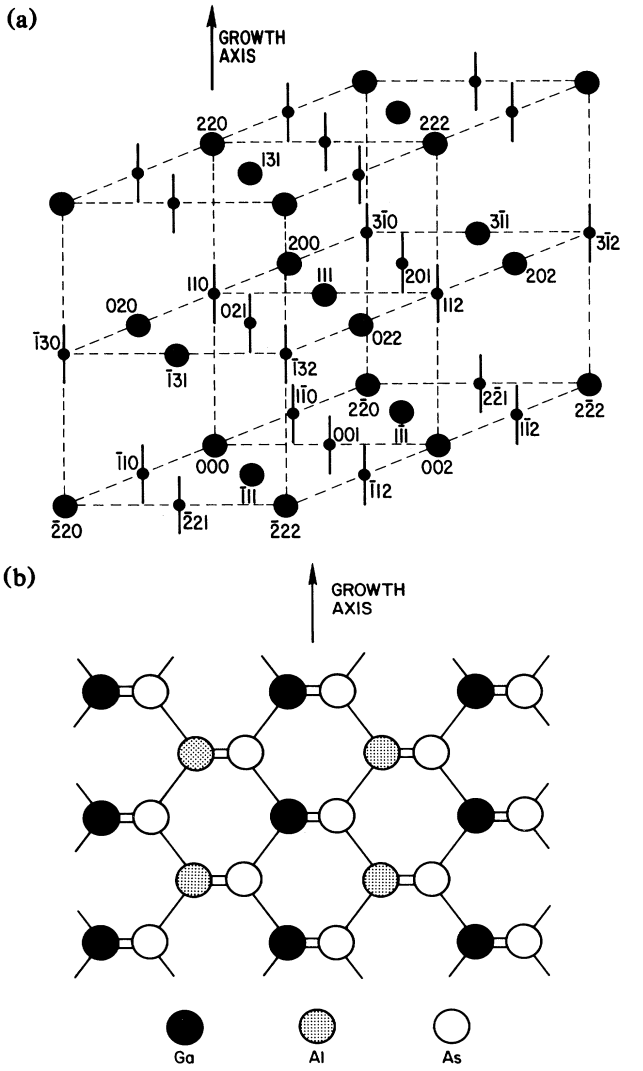

FIG. 2. (a) Reciprocal lattice of an ordered $Al_xGa_{1-x}As$ crystal grown along the [110] direction. Large closed circles represent the Bragg reflections and small closed circles are superstructure reflections. (b) Schematic diagram of a perfect long-range order in $Al_{0.5}Ga_{0.5}As$.

The superstructure reflections and streaks observed from $Al_xGa_{1-x}As$ alloys grown along the [110] direction are plotted in a three-dimensional reciprocal lattice in Fig. 2(a). Note that only those forbidden reflections with *hkl* indices such that $h+k=$ even and $k+l=$ odd are observed. In other words, *hkl* are (odd,odd,even) or (even,even,odd). For instance, 001 is observed [Fig. 1(a)] but 100 or 010 is not [Fig. 1(b)]. This particular set of superstructure reflections is allowed only if a long-range order exists in the crystal with the sites 0,0,0 and $\frac{1}{2},\frac{1}{2},0$ in each unit cell preferred by Ga atoms and the sites $\frac{1}{2},0,\frac{1}{2}$ and $0,\frac{1}{2},\frac{1}{2}$ preferred by Al atoms. A perfectly ordered structure of this type is shown schematically in Fig. 2(b) for $Al_{0.5}Ga_{0.5}As$. The structure consists of alternating AlAs and GaAs monolayers when viewed along either the [110] growth direction or the [001] direction normal to the growth axis. The ordered structure should have a tetragonal symmetry with [001] as its *c* axis as in an ordered CuAu I structure,[5] but the deviation from the cubic cell is too small to be detected from the electron diffraction patterns. Each As atom in this perfectly ordered structure is bonded to two Ga atoms and two Al atoms. However, the long-range order observed in all the crystals grown in this study, regardless of composition, is never perfect, i.e., only part of the Ga or Al sites are correctly occupied. Kinematically the structure factor of the superstructure reflections from a partial long-range order of this type can be expressed as[6]

$$F=2S(f_{\mathrm{Ga}}-f_{\mathrm{Al}}),$$

where f_{Ga} and f_{Al} are atomic scattering factors of Ga and Al, respectively, and S is a long-range order

parameter with a value ranging from 0 to 1 depending on the degree of order. For a perfectly ordered structure $S=1$, and for a completely random arrangement $S=0$. The parameter S can be expressed as[6]

$$S = r_{Ga} + r_{Al} - 1,$$

where r_{Ga} and r_{Al} are fractions of Ga sites and Al sites that are occupied by the preferred atom. The strongest superstructure reflections are observed from the $Al_{0.75}Ga_{0.25}As$ alloy grown at 700 °C, which can have a maximum S value of 0.5. Since the observed superstructure intensity is proportional to S^2, the S value of $Al_{0.5}Ga_{0.5}As$ grown at 650 °C, which exhibits only about a half of the above superstructure intensities, is estimated to be $\lesssim 0.3$.

Consider a sequence of (110) planes . . .GaAlGaAlGaAl. . . in an ordered crystal along the [110] growth direction. A local perturbation such as . . .AlGaAlAlGaAl. . . or . . .GaAlGaGaAlGa. . . is likely to happen in a growth fluctuation, which in effect creates a flat antiphase boundary normal to the growth direction. The appearance of streaks and the broadening of the superstructure reflections along the growth direction [Fig. 1(b)] suggest the presence of a high density of these boundaries. Thus the structure we observed is a limited form of long-range order in the sense that it is well ordered in two dimensions but the range of order is much less along the growth direction.

The same superstructure reflections with weak intensities are also observed in $Al_xGa_{1-x}As$ films grown on (100) GaAs substrates at specific compositions and temperatures (Table I). Diffraction data indicate that there are two orientations of ordered arrangement present simultaneously in the ordered crystal with their tetragonal c axes normal to each other and to the growth axis. The fact that the long-range order along [010] or [001] occurs at all when the growth is in the [100] direction indicates that kinetic effects cannot explain the phenomenon.

A structure similar to that described above is observed in a 0.5-μm-thick $Al_{0.3}Ga_{0.7}As$ film grown on (110) GaAs substrate by MBE at 600 °C. This film was grown at a growth rate of 0.3 μm/h with a V/III flux ratio of ~ 10 without substrate rotation. A high-resolution cross-sectional, bright-field electron micrograph of this film shows striae of alternating bright and dark lines normal to the growth direction. The width of each image line is about 0.5 nm (Fig. 3). According to our image simulation using a multislice method and the microscope parameters and the bright-field imaging condition used in Fig. 3, a segregated AlAs (110) monolayer in a GaAs matrix imaged in cross section from a 16-nm-thick sample would appear as a half-intensity dark line with width about 0.5 nm. The image decreases its contrast and turns into a bright line of the same width as the cross-sectional sample thickness

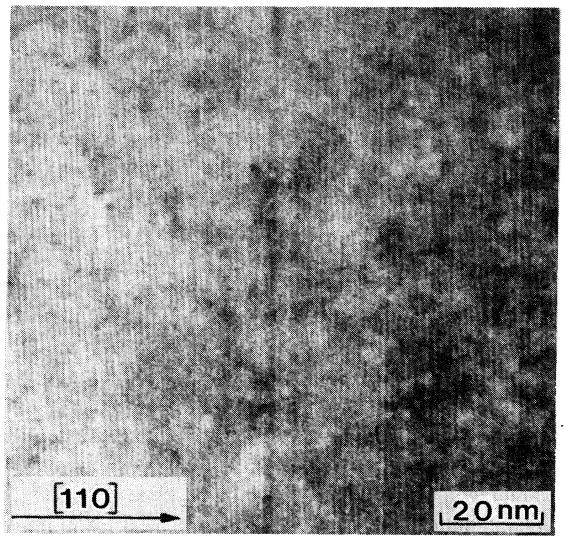

FIG. 3. Bright-field cross-sectional image of a $Al_{0.3}Ga_{0.7}As$ film grown on (110) GaAs by MBE at 600 °C.

increases from 16 nm to more than 30 nm. The simulated images of a segregated GaAs monolayer in a AlAs matrix have very similar features except that the image contrast is reversed. Thus we can interpret the contrast in Fig. 3 as from segregated AlAs and GaAs (or highly Al-rich and Ga-rich) monolayers. The scale of this segregated structure is much finer than that reported previously.[7] Close examination of Fig. 3 indicates that the stacking of these segregated monolayers is not periodic along the growth direction. The diffraction pattern from this sample shows only intensity streaks from the segregated monolayers but no intensity peaks at the 001 superstructure positions. Thus along the growth direction only a short-range order exists. A crystal with higher degree of order may be possible by MBE at some other growth conditions and compositions, which still remain to be explored.

All these observations on MOCVD- or MBE-grown $Al_xGa_{1-x}As$ crystals demonstrate the presence of a strong tendency toward an ordered state which, once reached, remains stable at temperatures below the growth temperature. The ordered structure in $Al_xGa_{1-x}As$ is different from the chalcopyrite structure commonly observed in the I-III-VI or II-IV-V compounds (e.g., $CuGaSe_2$, $ZnGeAs_2$),[8] but the latter is somewhat similar to the ordered $Al_xGa_{1-x}As$ in the sense that each column-V (or -VI) atom is bonded to two column-II and two column-IV atoms (or two column-I and two column-III atoms). On the basis of our diffraction results we suggest that the ordered arrangement of Ga and Al atoms in $Al_xGa_{1-x}As$ is an equilibrium state with a free energy lower than but very close to that of the disordered state. A lower-

free-energy state associated with long-range order may exist in other III-V alloys. The ordered state in $Al_xGa_{1-x}As$ is reached through the surface diffusion of Ga and Al atoms during the high-temperature growth. A possible mechanism involves constant segregation of the top layer on the growth surface into AlAs and GaAs areas, and as the growth continues the next GaAs overlayer grows on AlAs areas and the AlAs overlayer on GaAs areas.

The ordering of the $Al_xGa_{1-x}As$ crystal is dependent on both growth temperature and alloy composition. As the AlAs mole fraction of the material is increased, the temperature corresponding to the most pronounced ordering also increases. Slightly above this temperature the long-range order ceases to exist and the crystal becomes thermally disordered (Table I). The ordered state cannot be reached at lower growth temperatures, probably because of insufficient surface mobilities of Al and Ga atoms during the growth. Surface mobility is generally higher on the atomically flat (110) surface than on the (100) surface. Consequently, the ordered structure can be produced over a wider range of growth temperature for the (110) growth as we have observed.

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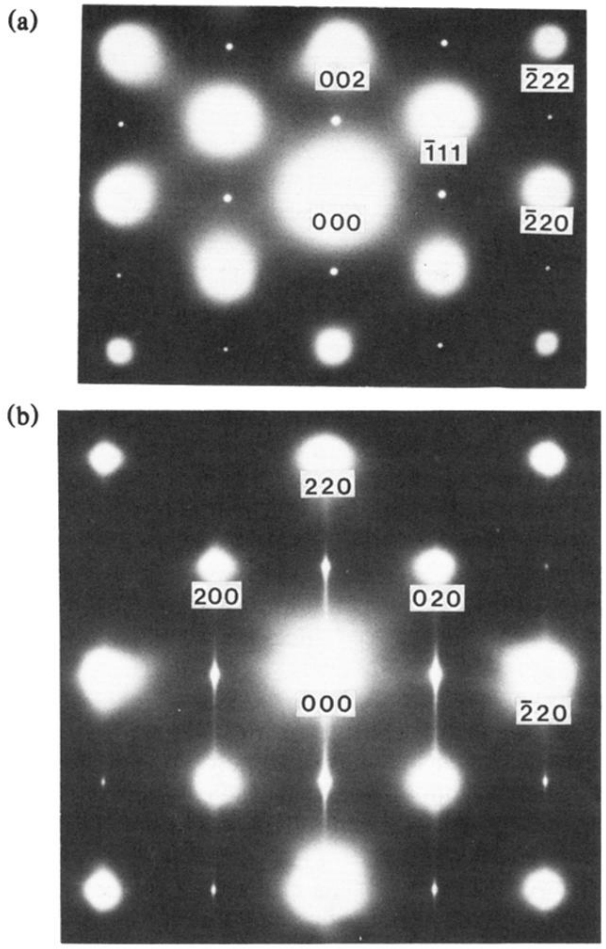

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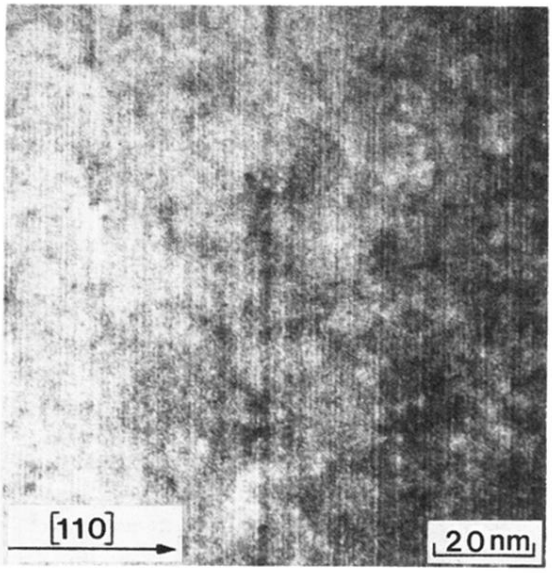

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