Title	Hopping conduction in GaAs layers grown by molecular-beam epitaxy at low temperatures
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Citation	Physical Review B, 65(16): 165311-1-165311-5
Issue Date	2002-04-04
Type	Journal Article
Text version	publisher
URL	http://hdl.handle.net/10119/4603
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PHYSICAL REVIEW B, VOLUME 65, 165311

Hopping conduction in GaAs layers grown by molecular-beam epitaxy at low temperatures

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(Received 21 September 2001; published 4 April 2002)

The electrical conductivity of GaAs layers grown by molecular-beam epitaxy at low temperatures was studied by using the van der Pauw method. The electrical conductivity of thick GaAs layers grown at temperatures above 200 °C changes with the concentration of antisite As atoms following the nearest-neighbor hopping model. From the dependence of the conductivity on the average spacing of antisite As atoms, the Bohr radius of the donor wave function in the hydrogen like model was estimated to be between 2.8 and 4.0 Å. The activation energy for hopping conduction changes inversely with the average distance of antisite As atoms. Enhanced incorporation of excess As occurs in the growth of ultrathin GaAs layers at low temperatures. The electrical resistivity of the ultrathin layers is reduced to nearly 1 Ω cm at room temperature by the enhanced incorporation. The activation energy for hopping conduction in the ultrathin layers is significantly lower than that expected from the inversely proportional relation with the average spacing of antisite As atoms.

DOI: 10.1103/PhysRevB.65.165311 PACS number(s): 81.05.Ea, 81.15.Hi, 71.30.+h, 72.20.−i

I. INTRODUCTION

A GaAs layer grown by molecular-beam epitaxy at a low temperature (LT GaAs) contains a high concentration of excess As as a form of point defects.[1] The majority of excess As point defects are antisite As atoms,[2] while a lower concentration of Ga vacancies were also found to exist.[3] The presence of other point defects such as interstitial As atoms and defect complexes has been suggested, but their concentrations, to our best knowledge, have not been experimentally determined to date. Antisite As atoms are known as deep donors, and their level is located around 0.75 eV below the conduction-band edge.[4] Ga vacancies are known as deep triple acceptors.[4] From the correlation of concentrations of excess As point defects,[5] a portion of antisite As atoms were found to be compensated by Ga vacancies and become singularly ionized atoms in undoped LT-GaAs layers, while all Ga vacancies are considered to be triply ionized.

An as-grown LT-GaAs layer exhibits relatively high electrical conductivity at room temperature but gains extremely high resistivity by postgrowth annealing. The electrical conduction in LT-GaAs has been investigated by a number of earlier studies,[1,3,6–12] among which Look *et al.* have extensively studied the conduction process in as-grown LT GaAs.[6] According to their study, the hopping conduction occurs among antisite As atoms and dominates the electrical conduction at room temperature, while at a higher measurement temperature the band conduction becomes significant due to thermal excitation of electrons from the antisite As states to the conduction band.[6]

In the 1950s and 1960s, numerous studies were carried out on impurity conduction in doped semiconductors.[13] It was shown that with an increase in impurity concentration the electrical conduction changes from hopping to metallic conduction, resulting in sharp changes in the electrical conductivity and other physical properties such as the dielectric constant. Such metal-insulator transitions, however, can be observed only at temperatures far below room temperature due to thermal excitation of carriers from shallow-impurity levels to conduction or valence bands at higher temperatures. In the case of LT-GaAs, on the other hand, the hopping conduction among antisite As atoms dominates even at room temperature due to the deep level of antisite As states. A metal-insulator transition, hence, may occur at room temperature in LT-GaAs, if the excess As concentration can significantly be increased from the concentration reported to date. In the present paper, we report results of a study that has been carried out in order to examine the possibility of realization of a metal-insulator transition in LT-GaAs. The results presented here include the analysis of hopping conduction in thick LT-GaAs layers on the basis of the nearest-neighbor hopping model and electrical conductivity of ultrathin LT-GaAs layers in which enhanced incorporation of excess As occurs.[14]

II. EXPERIMENT

LT-GaAs layers were grown by utilizing a conventional molecular-beam epitaxy system. Semi-insulating epiready (100)GaAs wafers were used as substrates and mounted on an Mo holder with indium. After desorption of an oxide layer of the substrate surface, the surface was annealed with the As flux for 10 min at 600 °C, followed by the growth of a GaAs buffer layer of a thickness of 1500 Å at 580 °C. After the growth of the buffer layer, the temperature of the sample was lowered to the point at which the low-temperature growth was carried out. The method of substrate-temperature measurement was described in an earlier report.[15] The growth rate of all LT-GaAs layers reported here is 0.9 μm/h, and their substrates were rotated during the growth in order to maintain uniform flux conditions over the growth planes. Thick LT-GaAs layers were grown to a thickness of 6400 Å under various flux conditions. Ultrathin LT-GaAs layers containing excess As were grown by utilizing one Ga cell and two As cells. The ultrathin layers containing excess As with a thickness of 12.5 Å were periodically incorporated into stoichiometric LT-GaAs layers at an interval of 100 Å by changing the As flux intensity during the growth. More de-

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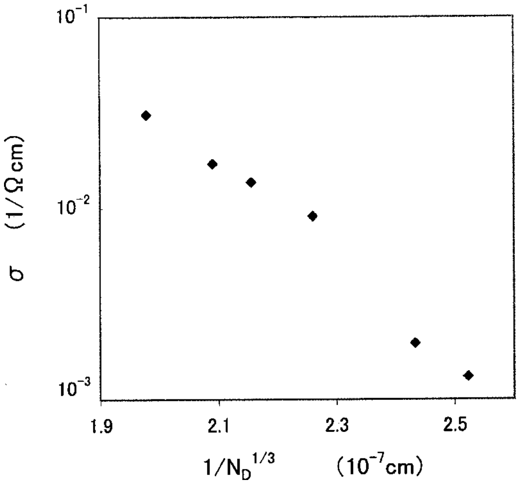

FIG. 1. Conductivity of thick LT-GaAs layers at room temperature as a function of the average spacing of antisite As atoms.

tails of the growth procedure of ultrathin layers were described in an earlier report.[14] X-ray-diffraction patterns of the LT-GaAs layers were obtained by using an x-ray diffractometer with a four-crystal monochrometer and Cu $K\alpha$ radiation. Cross-sectional images of the LT-GaAs layers were observed with a 300-kV transmission electron microscope (TEM).

A square 5×5 mm sample was cut for the van der Pauw measurement, and an In contact was made at each corner. For the LT-GaAs layers grown at temperatures above 200 °C the samples were annealed at 300 °C in a nitrogen atmosphere in order to obtain good ohmic contacts. It was found that the resistivity of the sample increased when the sample was annealed at a temperature higher than 300 °C, which may be attributed to rearrangements of excess As point defects due to the annealing. For the LT-GaAs layers grown at temperatures below 200 °C, no annealing was done, but good ohmic contacts were obtained in these samples.

III. RESULTS AND DISCUSSION

Resistivity measurements were made with LT-GaAs layers remaining on substrates whose thicknesses were 0.6 mm. The contribution of the electrical conduction through the substrate to the measured resistivity of LT-GaAs layers is, however, negligible because of very high resistivity of the substrate, which is on the order of 10^7 Ω cm at room temperature. The sheet resistance of a 5×5 mm substrate sample with a 1500 Å thick buffer layer on it is 8.0×10^7 Ω at room temperature, while sheet resistance of all LT-GaAs samples including ultrathin LT-GaAs samples are lower than 1.5×10^6 Ω at room temperature. No correction, therefore, was made for the contribution of the substrate and buffer layers to the measured resistivity.

Figure 1 shows the conductivity of 6400-Å thick LT-GaAs layers at room temperature as a function of the average spacing of antisite As atoms. Concentrations of antisite As atoms of LT-GaAs layers were derived by using the relation to the change of lattice spacings of LT-GaAs layers,[2] which were estimated with the x-ray-diffraction patterns. The measured conductivity of these LT-GaAs layers does not depend on their growth temperatures, which range between 200 °C and 270 °C, but directly depends on the concentration of excess As atoms; LT-GaAs layers grown at different temperatures but containing almost identical concentrations of antisite As atoms have nearly equal resistivity.

Figure 1 shows a nearly linear relation of logarithm of the conductivity with the average spacing of antisite As atoms, which is expected from the nearest-neighbor hopping model. The conductivity in the nearest-neighbor hopping model[16] is given by

$$\sigma = Ce^{-\gamma/aN_D^{1/3}}e^{-\varepsilon/kT}, \tag{1}$$

where C and γ are constants, a is the Bohr radius of the donor wave function in the hydrogenlike model, N_D is the donor concentration, and ε is the activation energy for electron hopping. According to Eq. (1), the Bohr radius a can be estimated from the slope of the linear change of the logarithm of σ. With the value 1.8 for the constant γ, which was suggested by Shklovskii,[16] the Bohr radius 2.8 Å is derived from all the data points in Fig. 1. Close inspection of Fig. 1 shows that the slope slightly changes from the range of the higher conductivity to the range of the lower conductivity. Four data points in the higher-conductivity range are aligned along a nearly straight line, while those in the lower-conductivity range deviate from it to a certain extent, which may be attributed to difficulty in making good ohmic contact in these low-conductivity samples. The Bohr radius estimated from four high-conductivity data points is 4.0 Å.

With the radii derived above, the critical donor concentration N_c for the metal-insulator transition can be estimated by using the relation

$$N_c^{1/3}a \approx 0.27. \tag{2}$$

This relation is applicable to uncompensated materials.[13] In the case of undoped LT-GaAs, a small portion of antisite As, less than 10%, is known to be positively ionized,[5] but to our best knowledge the role of these ionized antisite As in the hopping conduction has not been clarified at present. Critical concentrations derived from the radii of the donor wave function, 2.8 and 4.0 Å with Eq. (3) are 6.5×10^{20} and 2.5×10^{20} cm^{-3}, respectively. These values are higher than but in the same order with the maximum concentration of antisite As atoms in a thick LT-GaAs layer, 1.2×10^{20} cm^{-3}, which has already been reported.[2]

Temperature dependence of the resistivity of selected LT-GaAs layers is shown in Fig. 2(a) in which the upper three lines were obtained from thick LT-GaAs layers. The lower three lines are the resistivity of ultrathin LT-GaAs layers, which will be explained later. The linear relation of $\ln\varrho$ with $1/T$, which is expected from Eq. (1), is seen for all samples in Fig. 2(a). In the lower-temperature range, the $1/T^{1/4}$ dependence of the variable range hopping model may be observed as reported in an earlier study of the electrical conductivity of LT-GaAs.[6]

In Fig. 2(b), activation energies derived from the temperature dependence of the resistivity of the three thick LT-GaAs layers are plotted as a function of the reciprocal of the aver-

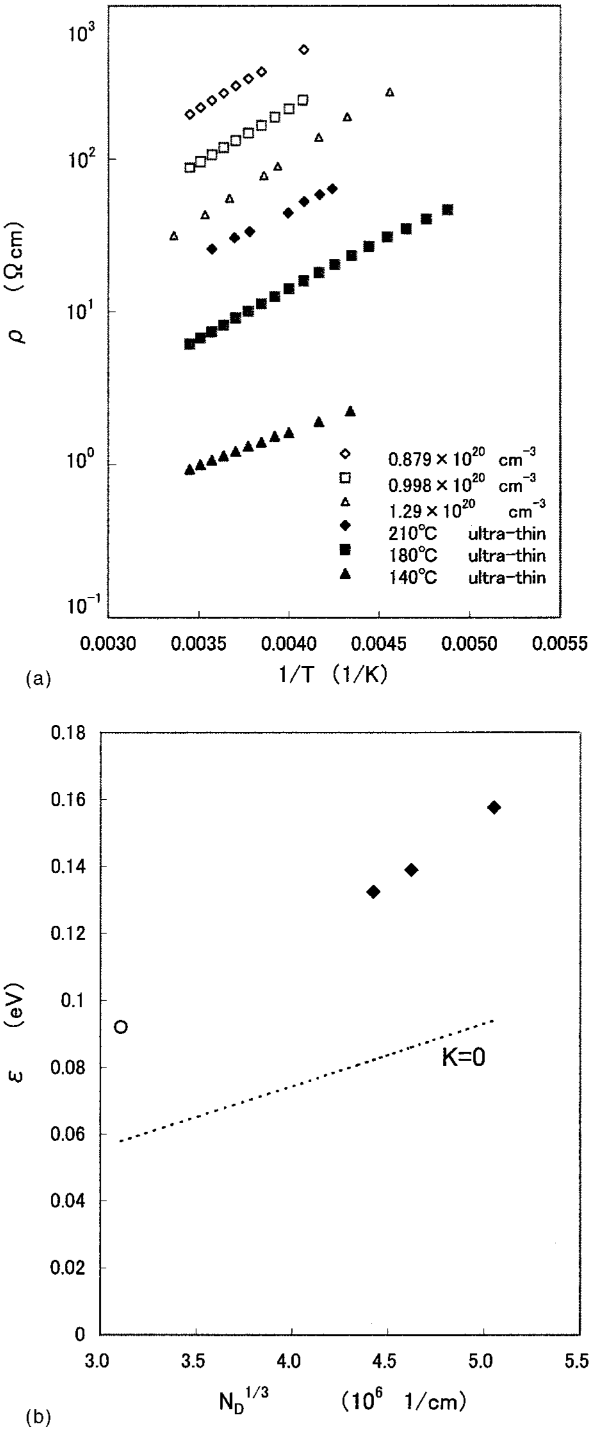

FIG. 2. (a) Temperature dependence of the resistivity of thick and ultrathin LT-GaAs layers. (b) Activation energy for hopping conduction in thick LT-GaAs layers as a function of the reciprocal of the average spacing of antisite As atoms. The data point denoted by an open circle is reported by Bliss *et al.* (Ref. 3).

age spacing of antisite As atoms. The activation energies were estimated by the method of least squares with errors of mean squares in the estimated activation energies being less than 0.0003 eV. In the figure the activation energy reported by Bliss *et al.*[3] is also plotted. As seen in Fig. 2(b), the activation energy is inversely proportional to the average spacing. Such an inversely proportional relation has been predicted by earlier theoretical studies on the impurity conduction of doped semiconductors.[17] The relation derived by Miller and Abrahams[18] is given by

$$\varepsilon=(e^2/4\pi\epsilon)(4\pi N_D/3)^{1/3}(1-1.35K^{1/2}), \qquad (3)$$

where ϵ is the dielectric constant and K is the degree of compensation. With the value for K being smaller than 0.1,[5] the activation energy can be roughly estimated by using Eq. (3) and can be compared with measured energies. In Fig. 2(b), the activation energy calculated with Eq. (3) by assuming that $K=0$ is shown by a broken line. Calculated values are smaller than but in the same order with the observed values. One may, therefore, consider that the model underlying Eq. (3) can predict the activation energy in the present case fairly well in spite of the relative simplicity of the model. Nearly linear relations seen in Figs. 1 and 2(b) suggest that the nearest-neighbor hopping model, which was originally developed for doped semiconductors, can be used for describing the electron hopping process among antisite As atoms in LT-GaAs in the temperature range around room temperature.

As explained earlier, the critical donor concentrations derived from Fig. 1 are higher than but in the same order with the maximum concentration of antisite As atoms, which has already been reported. The concentration of antisite As atoms in a LT-GaAs layer increases with lowering of the growth temperature under a high As flux condition. The increase of the concentration, however, is restrained at growth temperatures below 200 °C,[15] and the growth of a thick single-crystalline LT-GaAs layer becomes difficult at lower temperatures. In a recent study we have found that the incorporation of excess As can be enhanced by the growth of ultrathin LT-GaAs layers.[14] According to the analysis of x-ray-diffraction patterns, the concentration of antisite As atoms in the ultrathin layers grown at a low temperature is more than twice the aforementioned maximum concentration. In the present study, we have grown ultrathin LT-GaAs layers at lower temperatures in order to further increase the concentration of antisite As atoms and measure their electrical resistivity.

Figure 3(a) is a cross-sectional bright field TEM image of periodic ultrathin LT-GaAs layers grown at 210 °C. In the image, 12.5 Å thick ultrathin layers appear as bright lines, while 100-Å thick nearly stoichiometric layers are seen as dark bands. Figure 3(b) is the 400 reflection in the x-ray-diffraction pattern of the same ultrathin layers. Two high-intensity peaks are the zero-order peak of the periodic structure and the 400 reflection of the substrate, and the low-intensity peak in the each side is the first-order satellite peak of the periodic structure. From the intensity of satellite peaks and the splitting of the zero-order peak from the substrate 400 peak, lattice spacings of (400) plans in the ultrathin layers and the 100-Å thick layers can be estimated, a procedure that has been described in a recent paper.[19] With the lattice spacings thus estimated, the concentration of antisite As atoms in each layer can be derived on the basis of the relation reported by Liu *et al.*[2] The concentration of antisite As atoms

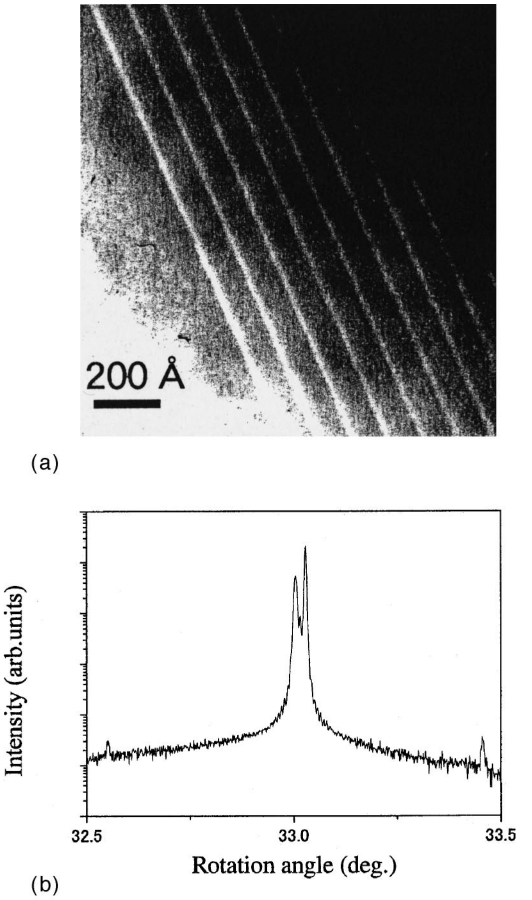

FIG. 3. (a) Cross-sectional bright field TEM image and (b) x-ray-diffraction pattern of a multilayer structure consisting of 12.5-Å thick ultrathin layers and 100-Å thick nearly stoichiometric layers that were grown at 210 °C.

in the ultrathin layers and 100-Å thick layers of the sample shown in Fig. 3 are 2.5×10^{20} and 2×10^{19} cm^{-3}, respectively.

In Fig. 2(a), the temperature dependence of the resistivity of ultrathin LT-GaAs layers grown at 210 °C, 180 °C, and 140 °C is shown. Estimated concentrations of antisite As atoms in the ultrathin layers grown at 180 °C and 140 °C are 2.7×10^{20} and 3.6×10^{20} cm^{-3}, respectively, while the concentrations of antisite As atoms in 100-Å thick layers of these two samples are lower than 5×10^{19} cm^{-3}. Because of the low concentrations of antisite As atoms in the 100-Å thick layers with which the conductivity changes in the manner shown in Fig. 1, the electrical conduction through 100-Å thick layers can be neglected in the estimation of the resistivity of ultrathin layers of these three samples; their resistivity was derived from measured sheet resistances of the samples by assuming that effective thicknesses of the samples were those of ultrathin layers.

As seen in Fig. 2(a), the resistivity of ultrathin layers is significantly reduced by lowering the growth temperature. The resistivity of the ultrathin layers grown at 140 °C is 0.9 Ω cm at room temperature. The low resistivity of the ultrathin layers is attributed to the high concentrations of antisite As atoms in these layers, but the simple extrapolation of the linear relation seen in Fig. 1 to the values of the ultrathin layers may not be possible because of their nearly two-dimensional structure. The growth of ultrathin layers at temperatures lower than 140 °C was attempted in order to further decrease the resistivity, but resulting layers were highly defective and exhibited high resistivity.

An important point noted in Fig. 2(a) is the reduction of slopes of the ultrathin layers from those of the thick LT-GaAs layers. If one assumes the nearest-neighbor hopping for the conduction in the ultrathin layers, the results imply the reduction of activation energies for hopping conduction in the ultrathin layers. The activation energies of the ultrathin layers grown at 210 °C, 180 °C, and 140 °C were estimated as 0.113, 0.123, and 0.085 eV, respectively, with errors of the mean squares being less than 0.0004 eV. This reduction in the activation energy with the increase in the concentration of antisite As atoms is in contrast to the change of the activation energy of the high-resistivity samples where the activation energy increases with the concentration of antisite As atoms. A gradual reduction of the activation energy for hopping conduction with increasing impurity concentration is known to occur in doped semiconductors where impurity concentrations approach the critical concentration for the metal-insulator transition.[20] Another possibility for the origin of the reduction in the slopes of the ultrathin layers is the transition from nearest-neighbor to variable range hopping. Because of the narrow temperature range of the resistivity measurements, it is difficult to distinguish between the $1/T$ and $1/T^{1/3}$ dependencies, the latter of which is expected for variable range hopping in ultrathin layers, with the present data. The variable range is known to occur at low temperatures, but it can also occur at high temperatures if the average spacing of impurities becomes comparable to the Bohr radius of the impurity wave function.[21] Regardless of either possibility of nearest-neighbor or variable range hopping, therefore, the present results of the ultrathin layers suggest that the metal-insulator transition may occur in LT-GaAs if the concentration of antisite As atoms can be a little further increased. In order to realize it, however, an additional method other than growth of ultrathin layers and lowering of the growth temperature may be needed.

ACKNOWLEDGEMENT

We would like to acknowledge the participation of A. Suda in the early part of the present study.

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