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Pressure study of metastability in $Ga_{1-x}Al_xAs$/GaAs:Si heterojunctions

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The variation of two-dimensional electron concentration (n_s) with temperature was studied in GaAs/$Ga_{1-x}Al_xAs$ ($x=0.3,0.35$) heterojunctions under true hydrostatic (gaseous helium) pressure. The metastable behavior of the sample, resulting from the large-lattice relaxation character of the Si donor is clearly seen below 120 K. The effects are reversible above $T_k=160$ K. The metastable character of the Si impurity makes it possible to lower the concentration by as much as tenfold at zero pressure. By appropriate gas-pressure cycling, any intermediate value of electron density is also obtainable. Using the gaseous medium we were able to vary the pressure at low temperatures, when the sample was in a metastable state. The most significant result obtained using this technique is that the concentration in this metastable state does not vary with pressure. We show that this is closely connected with the pressure independence of the band-gap offset ΔE_c.

INTRODUCTION

Many works in the literature are devoted to the properties of the donors controlling carrier concentration in $Ga_{1-x}Al_xAs$, such as Se, Te, Sn, and particularly Si, which is used as a dopant in the GaAs/GaAlAs modulation-doping structures. Studies on bulk samples with different Al contents as well as on samples under pressure have revealed that these donors can behave as shallow or deep donors depending on the relative positions of the Γ,L,X band minima.[1,2] The striking property of GaAlAs materials doped with these donors is the persistent photoconductivity (PPC) observed in the samples with $x>0.25$ and, under pressure, in the samples with lower x, i.e., in the cases where the deep level dominates.[3] It appears to be well established that this phenomenon is due to deep-level photoionization which becomes irreversible below a certain temperature. Recent studies have shown that deep and shallow levels coexist, and that their sum is equal to the concentration of the donors introduced.[4-6]

All the above-mentioned findings can be satisfactorily explained by a model of a donor center introducing several electron levels associated with different conduction-band minima, some of which exhibit large lattice relaxation (LLR).[6-8] In our case, the LLR level is associated with the L minimum.[7] The energy barrier for thermal transition of the electrons, implied by LLR, explains the essential feature determining the metastable character of the center: the thermally activated capture cross section. The barrier results in a lowering of the capture rate as the temperature decreases. Below a certain temperature the transitions between the LLR level and the conduction band become extremely slow (compared to measurement time). This means that the thermodynamic equilibrium occupancy of this level cannot be attained. It becomes metastable and the free-electron density is controlled by other levels. This change in processes governing the distribution of carriers results in a change in the temperature dependence of the electron concentration, which occurs at about 120 K in GaAlAs:Si samples. Above this temperature, the free-electron density is thermally activated and the activation energy depends on the deep-level position. At low temperatures, however, the temperature dependence is characteristic for shallow-level controlled density. Some authors misinterpret this variation of the electron activation energy as "saturation" of deep donors.[1] This leads to an erroneous application of the carrier statistics in determining the position of the Si level. If the existence of a constant value of the carrier concentration at low temperatures is correlated with the total ionization of an independent shallow donor, the saturation value would be the same whatever the depth of the deep level. However, if saturation value is due to a cessation of transitions to the deep level, the carrier concentration would be equal to the concentration of ionized donors at the critical temperature and would thus depend on the depth of the deep level. The change of the donor energy under hydrostatic pressure can be used to demonstrate unambiguously the metastable character of the deep level. We will show that the latter case corresponds to the actual situation in GaAlAs. When we are dealing with a metastable level the deviation from equilibrium concentration can be considerable when the sample is "frozen" at some pressure and the pressure is then varied. This makes it easy to observe the time-dependent phenomena when the temperature is raised sufficiently to make the transitions possible. The experimental procedure has been used with InSb: transport

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measurements under pressure were used to develop an accurate model of the main defect responsible for metastable properties.[9] The main parameters characterizing metastable behavior, i.e., the activation energies for capture and thermal emission cross sections, were determined in kinetic studies under pressure. To perform these pressure experiments it is necessary to vary the pressure at low temperatures, which is only possible in gas-pressure systems. This explains why metastability phenomena have not been observed in pressure studies on the transport properties of GaAs and GaAlAs in liquid-cell pressure systems.

Because the effect of pressure is similar to that induced by an increase in the Al content, pressure experiments on bulk GaAlAs with $x > 30\%$ can involve difficulties similar to those occurring in the study of high x values: the transport measurements do not give reliable results at temperatures lower than 100–150 K.[1] This is due to a decrease in mobility related to the electron transfer into L or X minima.

We show in this paper that it is possible to avoid these difficulties by studying the GaAs/GaAlAs heterostructures in which the density of two-dimensional (2D) electrons in the GaAs layer is strictly related to the properties of parent donors located in bulk GaAlAs. Since 2D carriers have high mobility, transport measurements are possible at low temperatures.

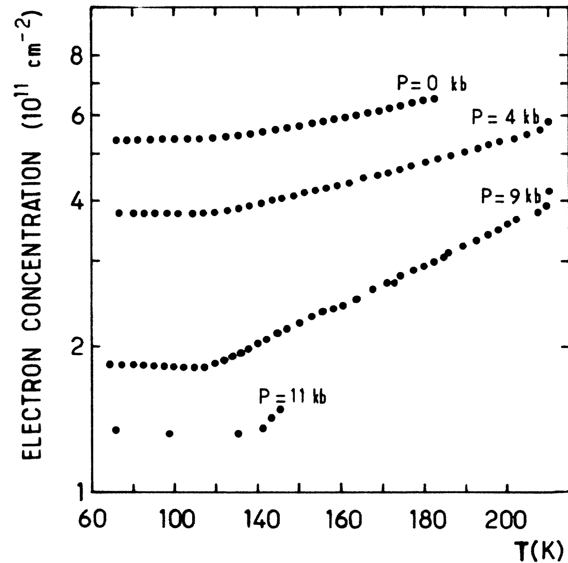

FIG. 1. The density of 2D electrons in the GaAs/$Ga_{0.65}Al_{0.35}As$ sample with 140-Å spacer as a function of temperature under different pressures. The results were obtained as the sample was cooled.

EXPERIMENTAL RESULTS AND DISCUSSION

The measured samples were heterostructures grown metalorganic chemical-vapor deposition (MOCVD) techniques. They consisted of a nominally undoped GaAs layer followed by an undoped GaAlAs layer [the spacer, which separates the parent donors from the two-dimensional electron gas (2DEG)], a Si-doped GaAlAs layer, and a thin cap layer to facilitate Ohmic contact formation. The Al contents in the GaAlAs layer was equal to 0.3 in one sample and 0.35 in two others, which differed by the spacer thickness: 90 and 140 Å. The spacer in the 30% sample has a width of 60 Å. A helium-gas pressure system was used, which made it possible to vary the pressure continuously over the whole temperature range studied (77–300 K). The density of the 2D electron gas confined at the GaAs side of the interface was determined from standard Hall-effect measurements. Figure 1 shows the variation of n_s as a function of temperature at several pressures in the sample with 35% Al. Only the results obtained on the sample with 140-Å spacer are reported (the measurements on the other one gave similar results). Analogous results for the sample with 30% Al are shown in Fig. 2. The results shown in Fig. 1 as well as the results marked by crosses in Fig. 2 were obtained as the sample was cooled from 300 to 77 K. The pressure at which the measurement was performed was increased at 300 K. The decrease of n_s with increasing pressure is due to increase of the binding energy of Si donor in GaAlAs layer, which lowers the Fermi level in the structure.[10] The slope of n_s vs T changed distinctly at about 120 K, as observed in GaAlAs bulk samples. It can be assumed that this is a consequence of the cessation of thermal transitions between the conduction band and the donor level, i.e., the passage to metastable conditions. This assumption is confirmed by the fact that the n_s cannot be changed at low temperatures: by reducing the pressure to zero at 77 K we did not obtain the value measured when the sample was

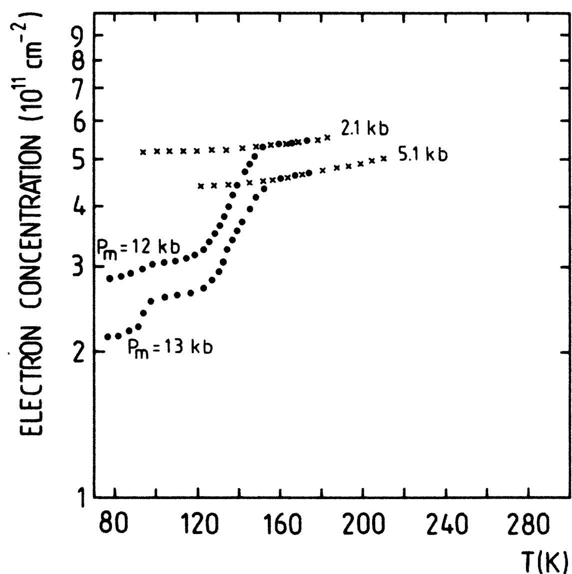

FIG. 2. The density of 2D electrons in GaAs/$Ga_{0.7}Al_{0.3}As$ as a function of temperature under different pressures. ×: measured as the sample was cooled. ●: sample heated from 77 K. P_m is the pressure at which the sample was cooled to obtain the initial metastable state. In the temperature ranges 90–100 K and 130–160 K the results were time dependent.

cooled at P=0. The values depended only on the pressure at which the sample was previously cooled. We denote this pressure by P_m. For example, the value of $n_s(P=0,T=77\text{ K})$ obtained after cooling the sample at 13.5 kbar was about ten times lower than that obtained when the sample was cooled without applying pressure. By adjusting the pressure P_m appropriately, any intermediate value of 2D electron density was obtainable. Consequently, pressure is a powerful tool for investigating the density-dependent properties of 2D electron gas such as mobility.[11]

The metastable character of the sample is clearly seen in Fig. 3, which shows n_s in the 35% sample with 140-Å spacer, measured while slowly heating the sample from 77 K (at a rate of about 1 K/min). The three presented curves were measured at $P=0$. Different initial metastable states of the sample have been obtained by increasing the pressure to P_m at high temperature ($T > 160$ K), cooling the sample at this pressure and then releasing the pressure to zero. Up to about 120 K, the electron density did not depend on temperature. Above this temperature, which approximately corresponds to the bending of the curves in Figs. 1 and 2, there was an increase in concentration with time. At 160 K, the values obtained with heating join those obtained by cooling the sample from 300 K. Above 160 K, the system was reversible and the time-dependent effect was not observed. Hence, in the temperature range 120–160 K, the equilibration times were comparable to measurement time.

The characteristic temperature, 160 K, is equal to the critical temperature above which PPC is no longer observed in Si-doped samples. We found the same characteristic temperature in all the samples irrespective of the pressure.

The heating curves measured in cases where the metastable state was obtained at the highest pressures show an additional threshold at about 85 K. This is most pronounced for the 30% sample initially cooled down at 13.5 kbar (Fig. 3). In this case carrier relaxation was observed in the range 85–100 K. This probably signifies that there is another metastable level, which is active only in the high-pressure range. A plausible hypothesis is that this level is an X-type level of the Si center.

The gas pressure system makes it possible to vary pressure at low temperatures, i.e., in the region where the 2D gas is metastable. By studying the 2DEG density as a function of pressure, direct information could be obtained concerning the pressure dependence of the conduction-band discontinuity ΔE_c, which is an important parameter of the heterojunction. Since the Si levels cannot regulate the free-electron concentration in the bulk below 120 K, this concentration remains constant regardless of the pressure. At a given temperature and as long as the Γ minimum dominates, the Fermi level in the bulk is not influenced by the pressure. In this situation, the position of the Fermi level in the quantum well would be changed only if the band discontinuity changes. The pressure dependences of 2DEG density measured at 77 K in three different metastable states of the 35% sample are shown in Fig. 4. No change in n_s is observed up to 10 kbar, which clearly indicates that ΔE_c is pressure independent. At pressures above 10 kbar, the X,L minima begin to modify the effective density of states. The Fermi level in the bulk is no longer constant. Its variation results in variation of the Fermi level in the well, which explains the decrease in n_s with the pressure.

In conclusion, we demonstrate here for the first time that the free-electron concentration in GaAs/$\text{Ga}_{1-x}\text{Al}_x\text{As}$, with $x=0.3$ and 0.35, has a metastable character below 120 K. This is a consequence of the large

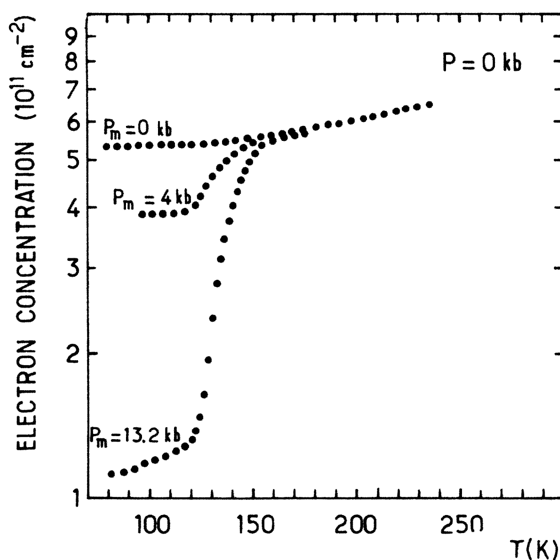

FIG. 3. 2DEG density vs increasing temperature in the 35% 140-Å spacer sample at atmospheric pressure. As in Fig. 2, P_m is the pressure at which the sample was cooled to obtain the initial metastable state.

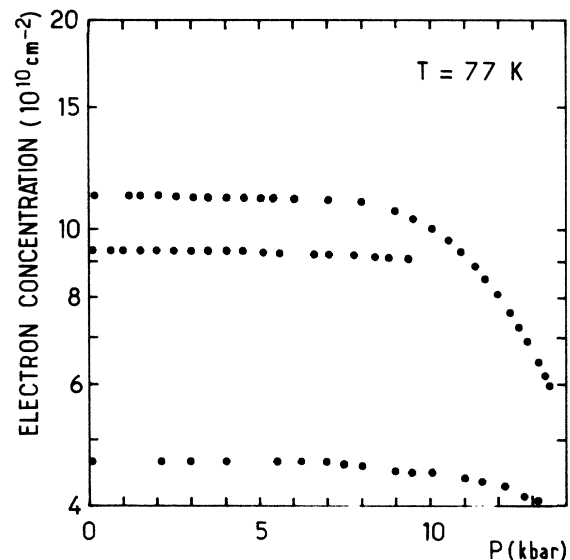

FIG. 4. Pressure dependences of 2D electron concentration measured at 77 K on 35% Al heterostructures, in different metastable states with lowered concentration. The upper curve: sample with 140-Å spacer. The two lower curves: 90-Å spacer sample. The "normal" concentration in this sample, obtained at 77 K without pressure, was equal to 5.4×10^{11} cm^{-2}.

lattice relaxation character of the Si deep level in GaAlAs layers. Our experiment showed that both the L and X levels can display this character. The invariance of the Fermi level observed in the quantum well, when pressure is varied in the metastable state, indicates that the band gap offset in GaAs/GaAlAs heterojunctions is pressure independent.

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[1]N. Chand, T. Henderson, J. Klem, W. T. Massekinh, R. Fisher, Y-C. Chang, and H. Morkoç, Phys. Rev. B **30**, 4481 (1984), and references therein.

[2]N. Lifshitz, A. Jayaraman, R. A. Logan, and H. C. Card, Phys. Rev. B **21**, 670 (1980).

[3]R. J. Nelson Appl. Phys. Lett. **31**, 351 (1977); M. Tachikawa, T. Fujisawa, H. Kukimoto, and A. Shibata, Jpn. J. Appl. Phys. **24**, L893 (1985).

[4]M. O. Watanabe, K. Morizuka, M. Mashita, Y. Ashizawa, and Y. Zohta, Jpn. J. Appl. Phys. **23**, L103 (1984).

[5]E. F. Schubert, J. Knecht, and K. Ploog, J. Phys. C **18**, L215 (1985).

[6]T. N. Theis, T. F. Kuech, L. F. Palmateer, and P. M. Mooney, in *Proceedings of the 6th International Symposium on GaAs and Related Compounds, Biarritz, 1984,* Institute of Physics Conference Proceedings No. 74 (IOP, Bristol, London, 1984), p. 241.

[7]T. N. Morgan, Phys. Rev. B **34**, 2664 (1986).

[8]M. Mizuta, M. Tachikawa, H. Kukimoto, and S. Minomura, Jpn. J. Appl. Phys. **24**, L143 (1985).

[9]L. Dmowski, M. Baj, P. Ioannides, and R. Piotrzkowski, Phys. Rev. B **26**, 4495 (1982).

[10]J. L. Robert, A. Raymond, C. Bousquet, and L. Konczewicz, Acta Phys. Pol. A **69**, 827 (1986).

[11]L. Konczewicz, E. Litwin-Staszewska, A. Maslowska, R. Piotrzkowski, and J. L. Robert (unpublished).