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Silicon doping and impurity profiles in Ga$_{0.47}$In$_{0.53}$As and Al$_{0.48}$In$_{0.52}$As grown by molecular beam epitaxy

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Silicon-doped n-type Ga$_{0.47}$In$_{0.53}$As and Al$_{0.48}$In$_{0.52}$As epitaxial layers lattice matched to InP substrates have been grown by molecular beam epitaxy. Doping levels up to $7 \times 10^{18}$ cm$^{-3}$ vary proportionally with the arrival rate of Si. For the same Si arrival rate, the carrier concentrations in both ternary epitaxial layers are identical. Mobility studies showed that the variations of electron mobility as a function of carrier concentration in Si-doped Ga$_{0.47}$In$_{0.53}$As are in good agreement with the theoretically calculated results involving the alloy scattering mechanism at both 77 and 300 K. This alloy scattering mechanism is attributed to the defects induced at lower growth temperature. Doping profile measurements by the differential capacitance technique show that very abrupt changes in carrier concentration can be realized in Si-doped Ga$_{0.47}$In$_{0.53}$As and Al$_{0.48}$In$_{0.52}$As and Sn-doped Al$_{0.48}$In$_{0.52}$As. In the case of Sn-doped Ga$_{0.47}$In$_{0.53}$As, the sharpness of the doping profile is limited by the surface segregation of Sn. Schottky barrier height on Ga$_{0.47}$In$_{0.53}$As was enhanced with the aid of a thin n-type Al$_{0.48}$In$_{0.52}$As surface layer.

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I. INTRODUCTION

Recently, molecular beam epitaxy (MBE) has become further advanced in its capabilities for the preparation of extremely uniform thin films with precision control of layer thickness, composition, and doping profiles of various III-V compound semiconductors. Al$_x$Ga$_{1-x}$As/GaAs thin-film devices grown by MBE with epitaxial layers in the submicron range exhibiting abrupt variation of carrier concentration, such as high electron mobility modulation-doped heterostructures, double heterostructure (DH) lasers, and photodetectors have been demonstrated. In the system of Ga$_{0.47}$In$_{0.53}$As and Al$_{0.48}$In$_{0.52}$As epitaxial layers lattice matched to InP substrates, the high electron mobility of Ga$_{0.47}$In$_{0.53}$As with a near band-gap emission of 1.65 eV at 300 K in conjunction with Al$_{0.48}$In$_{0.52}$As having a large band gap of $\sim 1.53$ eV, make this system very attractive for high-speed microwave devices and long wavelength fiber optical communication applications.

In order to fabricate devices with abrupt doping profiles in the micron range, dopants with minimum surface segregation during growth are required. For most MBE-grown III-V compound semiconductors, Sn and Si are the conventional n-type dopants. However, an abrupt doping profile in GaAs can only be obtained with a Si dopant.

In this work, we have studied the doping and electrical properties of Si-doped Ga$_{0.47}$In$_{0.53}$As and Al$_{0.48}$In$_{0.52}$As layers uniformly grown on InP substrates by MBE. The measured Hall electron mobilities in Ga$_{0.47}$In$_{0.53}$As were analyzed and compared with those grown by liquid phase epitaxy (LPE) and organometallic chemical vapor deposition (OM-CVD). The doping profiles obtained with Sn and Si dopants in Ga$_{0.47}$In$_{0.53}$As and Al$_{0.48}$In$_{0.52}$As epitaxial layers with stepwise changes in dopant beam intensities were studied by the differential capacitance technique. The Schottky barriers necessary for the doping profile measurements on the Ga$_{0.47}$In$_{0.53}$As epitaxial layer were enhanced with a very thin ($< 1000 \AA$) n-type Al$_{0.48}$In$_{0.52}$As epitaxial surface layer.

II. EXPERIMENTAL PROCEDURE

The MBE system used in this study is similar to the one described previously. On the source flange of the growth chamber, seven effusion cells are mounted with the orifice tilting upward between 5 and 32° above the horizontal plane. The orifice of each cell is 2.5 cm in diameter and is located 12 cm from the substrate. All crucibles are made of pyrolytic BN and contain high-purity elemental sources of Al, In, Ga, As, Be, Si, and Sn. The actual temperature of each effusion cell was monitored with thermocouples touching the bottom of the crucible and calibrated with an ir pyrometer looking into the crucible through view ports. The substrate holder can accommodate a wafer with a 2-in. diameter and can rotate continuously at a speed of from 0.1 to 5 rpm during growth. The results reported in this paper were obtained with a rotation speed of 3 rpm. A liquid nitrogen cooled shroud is used to enclose the entire growth area in order to minimize the residual water vapor and carbon-containing gases in the vacuum chamber.

Both Ga$_{1-x}$In$_x$As and Al$_{1-x}$In$_x$As layers were grown on (100) oriented InP substrates which were either semi-insulating Fe-doped for Hall measurements or n-type S-doped...
for doping profile studies. The substrate was prepared according to the procedures described earlier. After a flash desorption of the surface oxide at \(\sim 500^\circ C\) under the exposure of an As beam, the epitaxial growth was carried out with a typical growth rate of \(\sim 2.5 \mu m/h\) for both \(Ga_{0.47}In_{0.53}\)As and \(Al_{0.48}In_{0.52}\)As. The maximum growth temperature of \(Ga_{1-x}In_x\)As epitaxial layers was limited by the incongruent evaporation of \(Ga, In,\) and \(As\) from the surface initiated around \(580^\circ C\). For the growth of \(Al_{1-x}In_x\)As layers, the maximum substrate temperature of \(\sim 530^\circ C\) was set to prevent formation of pits on the surface. At the onset of growth, lattice mismatching between the epitaxial layer and the InP substrate was monitored with high-energy electron diffraction (HEED). X-ray diffraction was used to determine the composition of the epilayers upon the completion of the growth. In all cases, the lattice match between the epilayer and the substrate is less than \(1 \times 10^{-3}\), which, according to Vegard's law, corresponds to a compositional variation of \(2\%\) from the lattice matched condition. Compositional variation in the lateral direction is negligibly small when grown with a rotating sample holder at a rotation speed of \(3\) rpm. During the growth, the As background pressure in the growth chamber was kept above \(1 \times 10^{-7}\) Torr to permit growth under an As-stabilized condition.

The doping and electrical properties of Si-doped \(Ga_{1-x}In_x\)As and \(Al_{1-x}In_x\)As epitaxial layers grown on Fe-doped InP substrates were measured by the Van der Pauw method. Ohmic contacts were made by alloying indium dots onto the epitaxial layer at \(400^\circ C\) for \(30\) sec in \(H_2\) ambient. The layer thicknesses used in this study were about \(3\ \mu m\).

Si and Sn doping profiles as a function of depth in the \(Ga_{1-x}In_x\)As and \(Al_{1-x}In_x\)As epitaxial layers grown on Sn-doped InP substrates were measured on reverse-biased Schottky barriers using a differential capacitance technique. The Schottky barriers were formed by evaporating Au through a Mo mask consisting of arrays of 1, 5, 10, and 20 mil-diam holes. The indium solder on the backside of the heavily doped substrate wafer used to hold the substrate during growth served as the ohmic contact. Mesa diodes were then formed by etching in a 5% \(Br_2\)-methanol solution and were measured with a differential capacitance feedback profiler.

### III. RESULTS

#### A. Si doping

The dependence of room-temperature electron concentration on the Si oven temperature for \(Ga_{0.47}In_{0.53}\)As and \(Al_{0.48}In_{0.52}\)As layers grown on InP substrates is shown in Fig. 1. The solid line in Fig. 1 represents the Si equilibrium vapor pressure as a function of \(1/T\). The slope of the vapor pressure curve agrees with \(1/T\) dependence of the electron concentration over the doping range from \(7 \times 10^{16}\) to \(7 \times 10^{18}\) cm\(^{-3}\) of both ternary systems. At doping levels close to \(10^{19}\) cm\(^{-3}\), no sign of dopant saturation is observed and the surface morphologies are identical compared to undoped layers using an interference contrast microscope. These suggest that, over the concentration range studied, the Si doping level is pro-

![FIG. 1. Electron concentration as a function of Si oven temperature. \(T_s\) for MBE-grown \(Ga_{0.47}In_{0.53}\)As and \(Al_{0.48}In_{0.52}\)As layers: The solid line represents the Si equilibrium vapor pressure curve.](image)

![FIG. 2. Hall mobilities as a function of carrier concentration for Si-doped \(Ga_{0.47}In_{0.53}\)As and \(Al_{0.48}In_{0.52}\)As layers. The solid lines are the experimental mobility results of MBE-grown Sn-doped \(Ga_{0.47}In_{0.53}\)As and \(Al_{0.48}In_{0.52}\)As layers (Ref. 15). The dashed curves are theoretical calculations on the electron Hall mobilities for \(Ga_{0.47}In_{0.53}\)As and \(Al_{0.48}In_{0.52}\)As with alloy scattering (Ref. 16).](image)
proportional to the Si arrival rate. This is further supported by the identical doping properties of Si in these two ternary compounds. Since the incorporation of Ga and Al in these two systems is equal, a similar incorporation rate of Si in both of these two systems is expected.

B. Transport properties

Figure 2 displays the electron Hall mobilities as a function of carrier concentration for Si-doped Ga_{0.47}In_{0.53}As and Al_{0.48}In_{0.52}As epitaxial layers grown by MBE. The measured mobility data are compared to the results of the MBE-grown Sn-doped Ga_{0.47}In_{0.53}As and Al_{0.48}In_{0.52}As layers represented by three curves as shown in Fig. 2. In Sn-doped Ga_{x}In_{1-x}As epitaxial layers, the electron mobilities coincide with the mobility variations of those Sn-doped layers at both 77 and 300 K. The room-temperature mobilities are lower than those in LPE layers. However, this mobility difference between MBE- and LPE-grown layers disappears at 77 K. These results of MBE-grown layers at both 77 and 300 K, as discussed in a previous paper, follow the theoretical calculations by Takeda and Sasaki when including alloy scattering. For LPE layers, the room-temperature mobility results coincide with the calculated values when the alloy scattering mechanism is excluded.

In a recent study, the electron mobilities of the S-doped Ga_{0.47}In_{0.53}As epitaxial layers grown by OM-CVD were compared with that of LPE layers; the OM-CVD layers exhibit similar properties to those in the MBE layers. This could possibly be attributed to the relatively deep centers which are ionized at 300 K, but filled at 77 K. Using the low-temperature photoluminescence (PL) technique, no positive evidence was obtained. However, such a center could be nonradiative. It was suggested that the lower room-temperature mobilities in OM-CVD samples compared to the LPE samples were related to the alloy scattering mechanism which depends on the different methods of crystal growth.

Comparing the above three different growth techniques, i.e., MBE, OM-CVD, and LPE, it is found that both MBE and OM-CVD growths were conducted at a temperature below 600 °C. For low growth temperatures, the surface mobilities of Ga and In atoms decrease. Thus, the resulting increase in native defects as well as the increased sticking probability for impurities would be expected to cause an increase in defects. PL measurements on Sn-doped GaAs and Al_2Ga_1-x_As grown by MBE show a decrease in PL intensity with decreasing substrate growth temperatures. The deep level transient spectroscopy (DLTS) measurements in n-Al_{0.52}Ga_{0.48}As Schottky barriers grown by MBE reveal a deep level which decreases by over an order of magnitude in concentration as the growth temperature is increased from 575 to 675 °C. Thus, it could be suggested that the additional scattering mechanism in MBE and OM-CVD samples at room temperature is probably due to the defects induced at the lower growth temperature.

For the Si-doped Al_{0.48}In_{0.52}As epitaxial layers grown by MBE, the variation of electron mobilities as a function of carrier concentration follows the mobility variations of those Sn-doped Al_{0.48}In_{0.52}As epilayers. For the same carrier concentration, the electron mobility in Ga_{0.47}In_{0.53}As is about six times higher than that of Al_{0.48}In_{0.52}As at room temperature.

C. Si and Sn doping profiles

The doping properties of Si and Sn dopants in MBE-grown Ga_{0.47}In_{0.53}As and Al_{0.48}In_{0.52}As were further studied by comparing the doping profiles consisting of stepwise changes in dopant beam intensity with the actual carrier profiles measured by the differential capacitance technique. In these structures, a 1.5-μm-thick n⁺(2 × 10^{18} cm⁻³) buffer layer was grown on the heavily S-doped (~2 × 10^{16} cm⁻³) substrate first. Then the dopant intensity was abruptly reduced at about 1.2 μm from the surface. Three narrow pulses of Si or Sn atoms were then deposited into the growing Ga_{x}In_{1-x}As or Al_{x}In_{1-x}As, each with a duration of time equivalent to the growth of 350 Å of Ga_{x}In_{1-x}As or Al_{x}In_{1-x}As. The width of the individual pulse was accurately controlled by opening and closing the mechanical shutters in front of the corresponding effusion cells. Since the Schottky barrier diodes on Ga_{0.47}In_{0.53}As for the doping profile measurements are difficult to make because of the very low barrier height (0.2–0.3 eV) due to the small band gap, an n-type Al_{0.48}In_{0.52}As layer less than 1000 Å was deposited on top of the Ga_{x}In_{1-x}As surface to enhance the barrier height. The carrier concentration in the Al_{0.48}In_{0.52}As surface layer was kept below 10^{16} cm⁻³ to ensure total depletion under reverse bias during measurements.

Figures 3, 4, and 5 show calculated and measured profiles of Si- and Sn-doped Al_{0.48}In_{0.52}As and Sn-doped Ga_{0.47}In_{0.53}As epitaxial layers, respectively. The square PL files of Ga_{0.47}In_{0.53}As and Al_{0.48}In_{0.52}As grown by MBE were further studied. Three narrow pulses of Si or Sn atoms were then deposited into the growing Ga_{0.47}In_{0.53}As or Al_{0.48}In_{0.52}As, each with a duration of time equivalent to the growth of 350 Å of Ga_{0.47}In_{0.53}As or Al_{0.48}In_{0.52}As. The width of the individual pulse was accurately controlled by opening and closing the mechanical shutters in front of the corresponding effusion cells. Since the Schottky barrier diodes on Ga_{0.47}In_{0.53}As for the doping profile measurements are difficult to make because of the very low barrier height (0.2–0.3 eV) due to the small band gap, an n-type Al_{0.48}In_{0.52}As layer less than 1000 Å was deposited on top of the Ga_{x}In_{1-x}As surface to enhance the barrier height. The carrier concentration in the Al_{0.48}In_{0.52}As surface layer was kept below 10^{16} cm⁻³ to ensure total depletion under reverse bias during measurements.

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![Figure 3. Measured doping profile of a Si-doped Al_{0.48}In_{0.52}As layer grown at a substrate temperature of 530 °C.](image-url)
be achieved as shown in Fig. 3. However, the measured doping profiles deviate from the ideal rectangular profiles due to the majority-carrier diffusion which limited the step sharpness in C-V measurements by several Debye lengths. For a carrier concentration of \(10^{19} \text{ cm}^{-3}\), the Debye lengths in Ga\(_{0.47}\)In\(_{0.53}\)As and Al\(_{0.48}\)In\(_{0.52}\)As can be calculated, and they are about 465 and 435 \(\text{Å}\), respectively. Moreover, it was demonstrated that different doping profiles can be measured in a sample depending on whether the position of the rectifying contact was on the high or low doped side. This would contribute to the slight asymmetry near the bottom of the profiles.

In the case of Sn-doped Al\(_{0.48}\)In\(_{0.52}\)As epitaxial layers grown at 530 °C, the measured doping profile is about the same as the Si-doped samples as shown in Fig. 4. For a 350-Å wide molecular beam pulse, the measured profile broadening in the Sn-doped sample compared with that of the Si-doped sample is much less than one Debye length. This indicates that, under the growth condition discussed, surface segregation of Sn in Al\(_{0.48}\)In\(_{0.52}\)As is negligibly small, and both Si and Sn can be used as n-type dopant in Al\(_{0.48}\)In\(_{0.52}\)As for the fabrication of devices with abrupt doping profiles.

For Ga\(_{0.47}\)In\(_{0.53}\)As epitaxial layers grown at 580 °C, the Sn doping characteristics are quite different from the Si-doped samples. As shown in Fig. 5, the measured carrier concentrations decrease more slowly after the dopant beam has cutoff and the background carrier concentration between pulses are an order of magnitude higher than it would be expected. This is similar to the Sn-doped GaAs layers and may also be attributed to a surface segregation effect which becomes in evidence at higher growth temperature. Although this temperature dependent effect is less serious than in the GaAs system, it is suggested that Sn is not an ideal n-type dopant in the fabrication of Ga\(_{0.47}\)In\(_{0.53}\)As devices with stepwise changes in doping concentration.

IV. SUMMARY

The doping properties of Si-doped Ga\(_{0.47}\)In\(_{0.53}\)As and Al\(_{0.48}\)In\(_{0.52}\)As epitaxial layers grown lattice matched to InP substrates by molecular beam epitaxy have been studied. Doping concentration up to \(7 \times 10^{18} \text{ cm}^{-3}\) can be easily controlled by varying the Si oven temperature. High electron mobilities have been obtained in these materials. The analysis of the measured Hall mobilities in MBE-grown Si-doped Ga\(_{0.47}\)In\(_{0.53}\)As epitaxial layers shows, similar to that of MBE-grown Sn-doped layers and OM-CVD grown S-doped layers, the pressure of an alloy scattering mechanism which may be due to the defects induced at lower growth temperature.

The Si and Sn doping profiles in MBE-grown Ga\(_{0.47}\)In\(_{0.53}\)As and Al\(_{0.48}\)In\(_{0.52}\)As epitaxial layers with stepwise change in doping beam intensities were also studied using the differential capacitance technique. In spite of the very low Schottky barrier height on Ga\(_{0.47}\)In\(_{0.53}\)As, the doping profiles can be measured in this material with the aid of a very thin (\(< 1000 \text{ Å}\)) n-type Al\(_{0.48}\)In\(_{0.52}\)As surface layer to enhance the barrier height. Very sharp profiles with peak to background free-carrier concentration ratio near two orders of magnitude can be achieved easily in both Ga\(_{0.47}\)In\(_{0.53}\)As and Al\(_{0.48}\)In\(_{0.52}\)As systems doped with Si. The ultimate sharpness of the profile is limited by the majority-carrier diffusion.

For Sn-doped Al\(_{0.48}\)In\(_{0.52}\)As epitaxial layers, doping profiles nearly as sharp as Si-doped layers can also be obtained. However, surface segregation of Sn was observed in Ga\(_{0.47}\)In\(_{0.53}\)As layers grown at 580 °C. These results indicated that in Al\(_{0.48}\)In\(_{0.52}\)As epitaxial layers, both Si and Sn can be used to provide abrupt doping profiles. On the other hand, extremely abrupt carrier profiles in n-type Ga\(_{0.47}\)In\(_{0.53}\)As layers can only be obtained with Si dopant.

FIG. 4. Measured doping profile of a Sn-doped Al\(_{0.48}\)In\(_{0.52}\)As layer grown at a substrate temperature of 530 °C.

FIG. 5. Measured doping profile of a Sn-doped Ga\(_{0.47}\)In\(_{0.53}\)As layer grown at a substrate temperature of 580 °C. It has a very thin \(< 1000 \text{ Å}\) n-type Al\(_{0.48}\)In\(_{0.52}\)As surface layer to enhance the Schottky barrier height.

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