Formation of semi-insulating InP through metallic Cu-rich precipitates

R. P. Leon
Department of Materials Science, University of California, Berkeley, California 94720

M. Kaminska
Department of Materials Science, University of California, Berkeley, California 94720
and Institute of Experimental Physics, Warsaw University, Hoza 69, 00-681 Warsaw, Poland

Kin Man Yu
Materials Science Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

E. R. Weber
Department of Materials Science, University of California, Berkeley, California 94720
and Materials Science Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
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A set of diffusion experiments of Cu in InP have shown that this semiconductor exhibits a transition to semi-insulating behavior after relatively low Cu diffusion temperatures. The study described here involves structural, ion-beam/channeling, magnetic, and electrical measurements. It was observed that most or all of the Cu precipitates form a Cu-In compound, that both originally *n*- and *p*-type InP become semi-insulating upon Cu diffusion, and that there is a negligible concentration of deep-level defects in Cu-doped InP. Further observations include an abnormal reduction in both electron and hole mobilities resulting from the introduction of Cu, and the occurrence of isolated pockets of conductive InP in otherwise semi-insulating material. The concurrence of these experimental observations can best be explained using the buried Schottky-barrier model instead of the commonly observed compensation by deep levels.

I. INTRODUCTION

The availability of highly resistive (10^7 Ω cm) InP substrates is technologically important.[1] In the absence of a native defect with midgap energy level(s) this is normally achieved with the introduction of transition metals that have a midgap level and a large enough solubility so that compensation of the residual shallow impurities is possible. In the case of Fe, which is the most commonly used impurity to make semi-insulating (SI) InP, a deep acceptor is introduced at E_c-0.65 eV, and this compensates the usually dominant shallow donors as long as the Fe concentration is larger than the concentration of donors. Problems with this compensation scheme include poor thermal stability and detrimental diffusion into the active layers of devices. Ti, which introduces a midgap donor level,[2] has a lower diffusivity, but the need to counterdope with *p*-type impurities introduces extra processing steps. Finding a way to make SI undoped InP would provide an attractive way to circumvent some of these problems; however, despite recent attempts to produce SI undoped InP,[3] no level analogous to EL2 has yet been identified in InP.

Recently, evidence for a new mechanism to induce SI behavior in semiconductors has been observed in GaAs grown with low-temperature molecular-beam epitaxy (MBE). In these GaAs layers, a lower-than-normal growth temperature permits introduction of a large amount of excess arsenic, creating a novel type of GaAs which can have as much as 1.5% excess arsenic.[4] A great part of this excess As is found in the form of antisite defects (As_{Ga}); upon annealing, however, the majority of the extra As forms precipitates, creating a high concentration of clusters, most of which can be identified as hexagonal As.[5,6] Based on the observation of As precipitates and of semi-insulating behavior in annealed low-temperature GaAs, it has been proposed[7] that creating SI material is possible if the concentration of metallic precipitates present in the semiconductor crystal is sufficiently large so that the space-charge regions that form when a metal and semiconductor are in intimate contact could overlap and deplete the material of free carriers. This situation could have the effect of making the semiconductor intrinsic. For highly doped material, it would then be necessary to have a large concentration of these precipitates, since the width of the space-charge region varies with the inverse square root of the carrier concentration.[8] For nominally undoped or lightly doped InP, the space-charge regions are expected to be of the order of $\frac{1}{2}$ μm, and a lower concentration of these precipitates would be sufficient to cause this carrier depletion.

Here we show that there is evidence indicating that the buried Schottky-barrier model has general applicability, since it offers the best explanation for a wide variety of experimental observations in this study of the behavior of Cu in InP. Examination of some of the results from the 1960s involving studies of the behavior of Cu in GaP also seems to indicate that the aforementioned model might explain the observed SI behavior of GaP:Cu.[9,10] Recent results of thermal stability studies done on InP:Cu (Ref.

11) show that this material maintains a very high resistivity even after annealing at 800 °C for several hours, so the good thermal stability of the SI properties of these samples shows promise for future technological application. The possibility that this mechanism has general scope could enable the introduction of a novel type of material for device application where high-resistivity substrates are desired.

II. EXPERIMENT

Nominally undoped, n-type ($8-9\times10^{15}/cm^3$) bulk InP crystals and Zn-doped p-type ($4\times10^{16}/cm^3$) InP wafers grown by the liquid-encapsulated Czochralski method were used in this study. The samples were cut, mechanically polished, degreased in baths of trichloroethene, acetone, and methanol, and then etched in a 5% bromine and methanol solution. Cu was evaporated on all sides of the samples using a resistive-type evaporator with base pressure in the mid 10^{-7} Torr. The samples were then placed in quartz ampules, evacuated to 10^{-7} Torr and sealed with an acetylene torch. A small measured amount of pure phosphorus was introduced in the ampule with the sample to maintain the equilibrium phosphorus overpressure at the chosen diffusion temperatures.

Samples were placed in a vertical furnace, and diffused for 2–36 h at temperatures ranging from 500 to 950 °C. After diffusion, the samples were rapidly quenched by dropping the ampules in diffusion pump oil that was kept at room temperature. Any residual metallic Cu was removed from the sample surface by mechanical polishing followed by an etch in the bromine and methanol solution.

Particle induced x-ray-emission (PIXE) analysis was used to determine the total concentration of Cu. PIXE measurements were calibrated with secondary-ion-mass spectroscopy (SIMS). These measurements gave the temperature dependence of Cu solubility in InP. In the samples with the most abundant concentration of Cu, PIXE was complemented with channeling studies done in the three main crystallographic orientations. 1.4-MeV protons produced by a Van de Graaff generator were used for the ion beam. A 40-μm aluminum absorber was placed in front of the Si (Li) detector to overcome the saturation of the x-ray detector due to the InP substrate L x rays.

Structural investigation of the samples was done using a JEOL 200CX transmission-electron microscope (TEM). For chemical analysis of the precipitates, energy-dispersive spectroscopy (EDS) was done using a Phillips 400 TEM with analytical capabilities.

Temperature-dependent Hall-effect measurements were made using a highly stable, low-current apparatus and a Van der Pauw geometry of the sample. Ohmic contacts to semi-insulating InP:Cu samples were made by evaporating 50 nm of Sb followed by 150 nm of Au, and then annealing for 10 min in a 90% N_2 and 10% H_2 atmosphere at 410 °C. Contacts to p-type samples were made by evaporating a Au-Zn-Au layered structure and using the same heat treatment. Standard Au-Ge contacts were adequate for conductive n-type InP samples.

Deep-level transient spectroscopy (DLTS) measurements were done using a deep-level spectrometer from SULA Technologies. Aluminum Schottky barriers were made to p-type InP:Cu that had been diffused at 600 °C, and n-type Schottky-barrier diodes were made by creating a thin oxide layer on an InP:Cu sample diffused at 590 °C and evaporating Sb on this surface.

Electron-paramagnetic-resonance (EPR) measurements were done using a commercial X-band spectrometer (Bruker) equipped with a helium-gas-flow cryostat, to obtain measurements between 6 and 300 K.

III. RESULTS

Cu has a large solubility in InP. Figure 1 shows the concentration of Cu in InP as a function of temperature, as measured by PIXE. Two Cu concentrations were also calibrated by using SIMS analysis. All InP:Cu samples used in this study were quenched after Cu diffusion.

The diffusivity of Cu in InP was measured by making use of an approximation using the solution of the diffusion equation in one dimension for a semi-infinite rod. This solution gives the concentration of the diffusing species, and it is useful for examining concentration profiles near the surface of a relatively thick sample:

$$\rho(x,t)=C_s-(C_s-C_0)\mathrm{erf}\left[\frac{x}{2\sqrt{(Dt)}}\right],$$

where C_s is the concentration at the surface, C_0 the background concentration, and D the diffusivity. This measurement was done by evaporating a thick layer of Cu on one end of a thin long rod of InP. Cu was then diffused at 900 °C for 5 min and at 700 °C for 20 min. The InP rod was then cut and slices were carefully measured, accounting for losses due to saw cutting. Cu concentrations in the slices were then measured using PIXE (calibrated with samples of known Cu concentrations). The

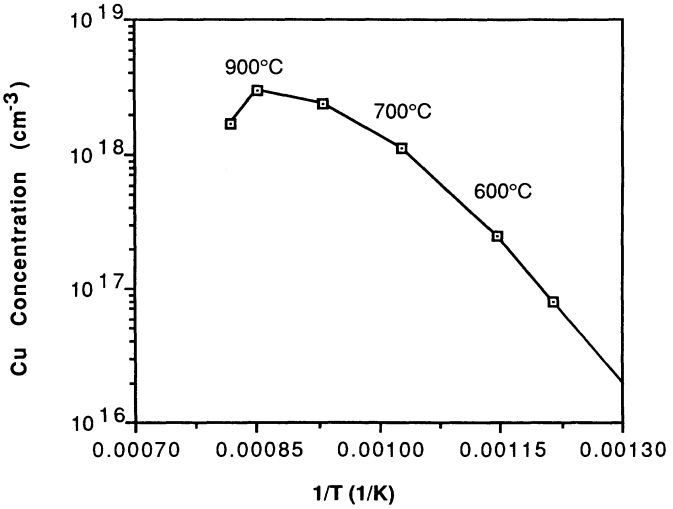

FIG. 1. Solubility of Cu in InP as a function of temperature. These data were obtained from PIXE and SIMS measurements. The maximum solubility occurs at 900 °C.

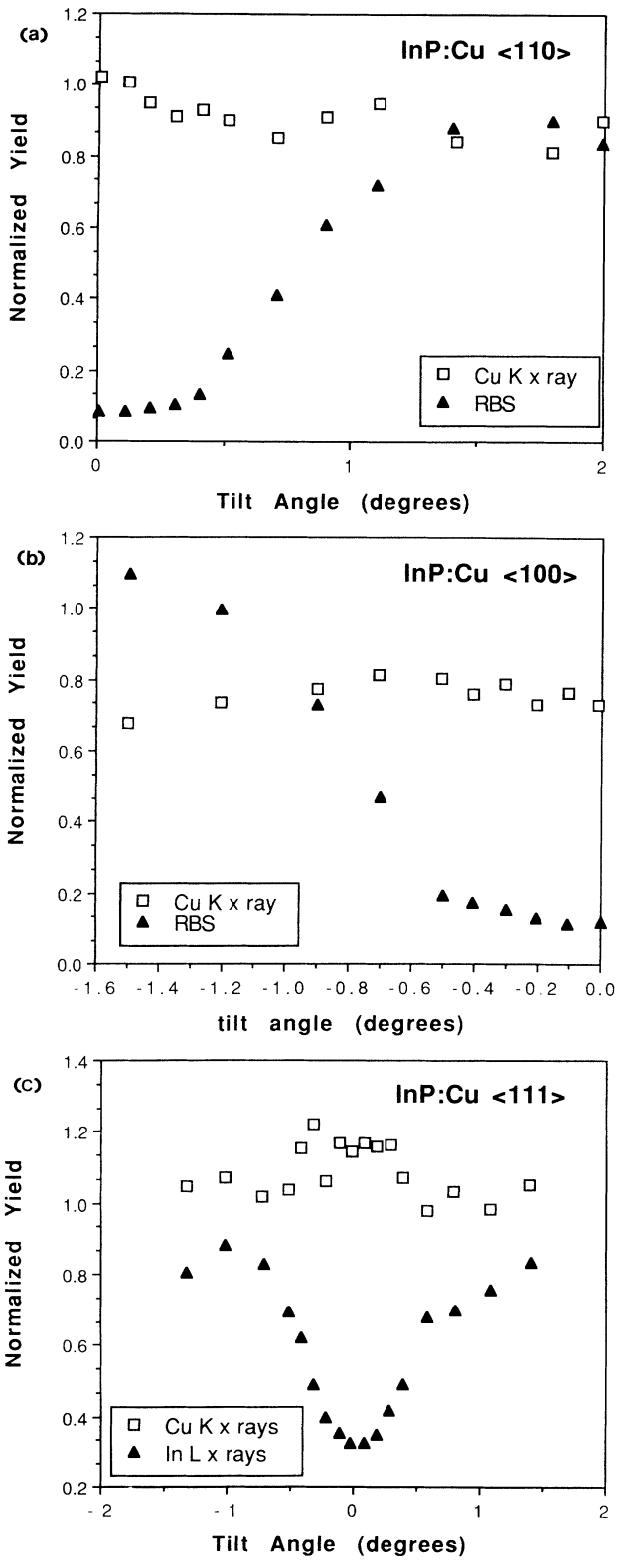

FIG. 2. Normalized x-ray impurity yield as a function of tilt angle for an InP:Cu sample that was diffused at 950°C and quenched. 1.4-MeV protons were used as the ion source. (a) X-ray yield in the ⟨110⟩, (b) ⟨100⟩, and (c) ⟨111⟩ directions. These impurity x-ray yields are compared with the RBS signal [⟨110⟩ and ⟨100⟩ scans] or the ln L x-ray [⟨111⟩ scan] coming from the host crystal.

diffusivities obtained this way were 1.3×10^{-5} cm^2/sec at 700°C and 3.6×10^{-5} cm^2/sec at 900°C. These values are close to the known values of Cu diffusivity in GaAs.[12]

Channeling was done in combination with PIXE, in order to determine the preferred lattice site of Cu in InP. Figure 2 shows the normalized Cu x-ray impurity yield as a function of tilt angle for an InP:Cu sample diffused at 950°C for 3 h and quenched. This is compared with the In L x-ray yield. The channeling scans for the ⟨100⟩, ⟨110⟩, and ⟨111⟩ orientations are shown, and it can be seen that they are qualitatively similar. The Cu x-ray signal does not follow the host signal as in the case of purely substitutional impurities. The Cu $K\alpha$ x-ray yield in the middle of the channels is close to what this yield is when the crystal is in a random orientation. This random distribution of Cu in the InP crystal, where the Cu atoms are blocking all channels, is normally observed when random precipitates are present, so the channeling data indicate that Cu-rich precipitates are formed. Furthermore, the high yield in the middle of the channels indicates that most of the Cu forms precipitates.

TEM examination of the same samples shows a large concentration of precipitates. Figure 3 shows a plan view TEM micrograph of one of the InP:Cu samples. The Moire fringes visible in these precipitates at certain orientations indicate that these precipitates are crystalline. Samples annealed at lower temperature were also examined, and precipitates were also found. The sizes of the precipitates varied from 5 to 50 nm. Energy-dispersive spectroscopy analysis shows these precipitates are In and Cu rich. Figure 4 shows x-ray energy scans taken from one of the precipitates shown in Fig. 3, and this scan is compared with another scan taken from an adjacent precipitate-free (InP matrix) region in the sample. Comparisons of these and other scans were used to determine the stoichiometry of these precipitates. Their stoichiometry corresponds to the monoclinic compound

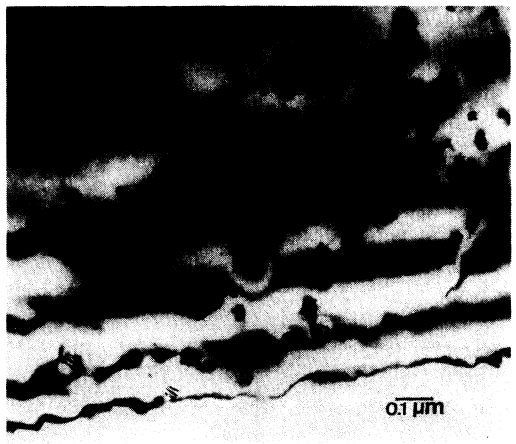

FIG. 3. Plan view TEM micrograph (two beam condition, bright field) of an InP:Cu sample that was diffused at 950°C. Samples diffused at lower temperatures also contain precipitates, but of smaller diameters. The Cu-rich precipitates showing Moire fringes can be clearly seen here.

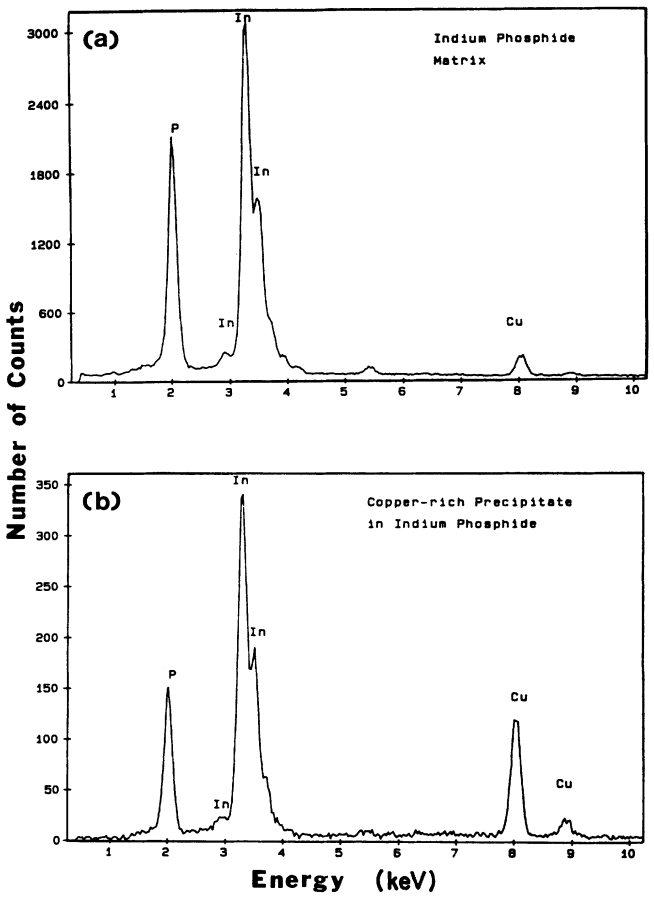

FIG. 4. EDS analysis of (a) the InP matrix and (b) one of the precipitates in Fig. 3. The precipitates are Cu and In rich.

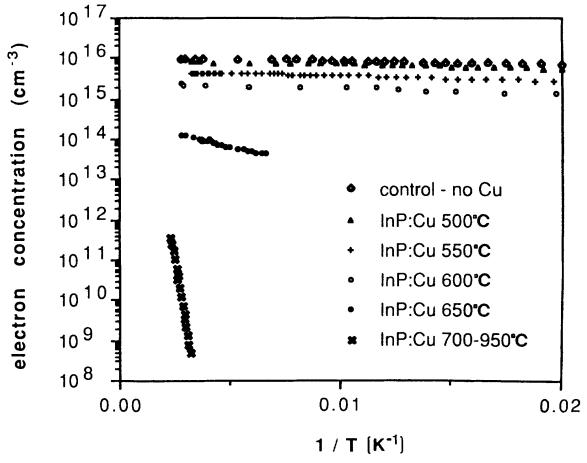

FIG. 5. Electron concentration as a function of inverse temperature for initially n-InP diffused with Cu at different temperatures. The decrease in electron concentration with increasing Cu concentration is apparent from this plot. The activation energy obtained from the semi-insulating samples in this plot is 0.65 eV.

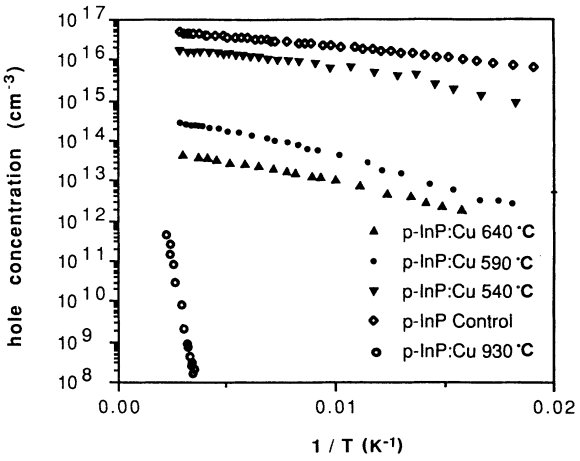

FIG. 6. Hole concentration as a function of inverse temperature for initially p-InP diffused with Cu at different temperatures. The activation energy obtained from the semi-insulating samples is also 0.65 eV.

$Cu_{11}In_9$.[13,14] On the other hand, preliminary structural analysis[11] shows that some of the precipitates exhibit the hexagonal phase[15] of $Cu_{16}In_9$. It is also observed that several phases might coexist, which is understandable, considering the many phases present in the In-Cu equilibrium phase[16] diagram in the above compositions and temperatures used in Cu diffusion. It is clear, however, that the precipitates are In-Cu compounds and are expected to be metallic.

Carrier concentration and resistivity measurements indicate that both n- and p-type InP samples exhibit very large decreases in conductivity after Cu diffusion. Figure 5 shows a plot of carrier concentration as a function of inverse temperature for samples that were originally n-type (nominally undoped). This plot shows the decrease

TABLE I. Room-temperature carrier concentrations after Cu diffusion at different temperatures in both initially n- and p-InP.

n-InP Initial concentration: 9×10^{15}	
Cu diffusion temperature	Electron concentration
500	8×10^{15}
550	4×10^{15}
600	2×10^{15}
700–950	5×10^{8} (SI)
p-InP Initial concentration: 5×10^{16}	
Cu diffusion temperature	Hole concentration
540	2×10^{16}
590	3×10^{14}
640	4×10^{13}
930	5×10^{8} (SI)

in electron concentration as a function of Cu diffusion temperature. Figure 6 shows similar plots for samples that were originally p type and that also became semi-insulating after Cu diffusion. The activation energy obtained from the slope of the semi-insulating samples in both of these plots gives a values of 0.60–0.65 eV for the samples that were initially n type, and 0.70–0.75 eV for the samples that were initially p type. These values are close to being half the band gap of InP. Table I shows a summary of the room-temperature (292 K) carrier concentrations that resulted from different temperature diffusions in both n and p samples.

DLTS measurements were done in order to determine if deep levels were responsible for this reduction in carrier concentration and subsequent semi-insulating behavior. Schottky diodes were made using both n- and p-type InP:Cu samples that were not yet semi-insulating but showed a lower carrier concentration than the control samples. Two hole traps were found in p-type InP:Cu; their energy levels are 0.30 and 0.47 eV above the valence band, but their concentration is only $1\times10^{12}/\text{cm}^3$. Figure 7 shows the two DLTS peaks for one of the time constants used and the corresponding Arrhenius plots for each peak. No other peaks were found in the p-type samples. No electron traps were found in n-type InP:Cu within a detection threshold of 1×10^{11} traps/cm^3.

Variable-temperature Hall mobility and resistivity measurements indicate unusual transport behavior for these InP:Cu samples. There was a very large drop in both electron and hole mobilities as a result of Cu diffusion. In n-type samples, the mobility at liquid-

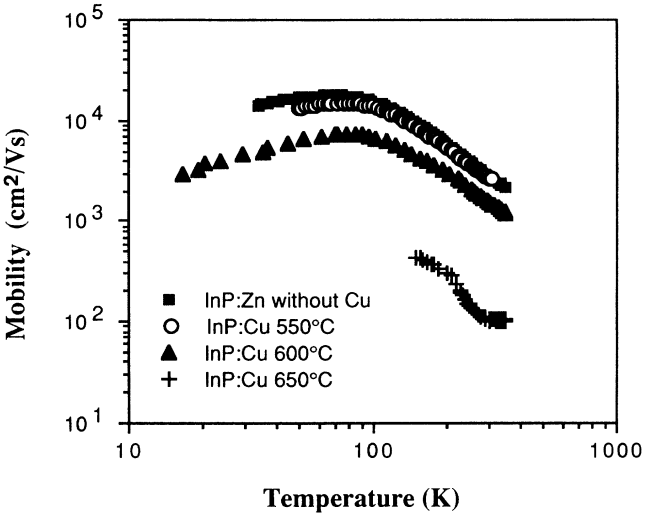

FIG. 8. Temperature dependence of the electron mobilities for n-InP:Cu samples with different Cu concentrations.

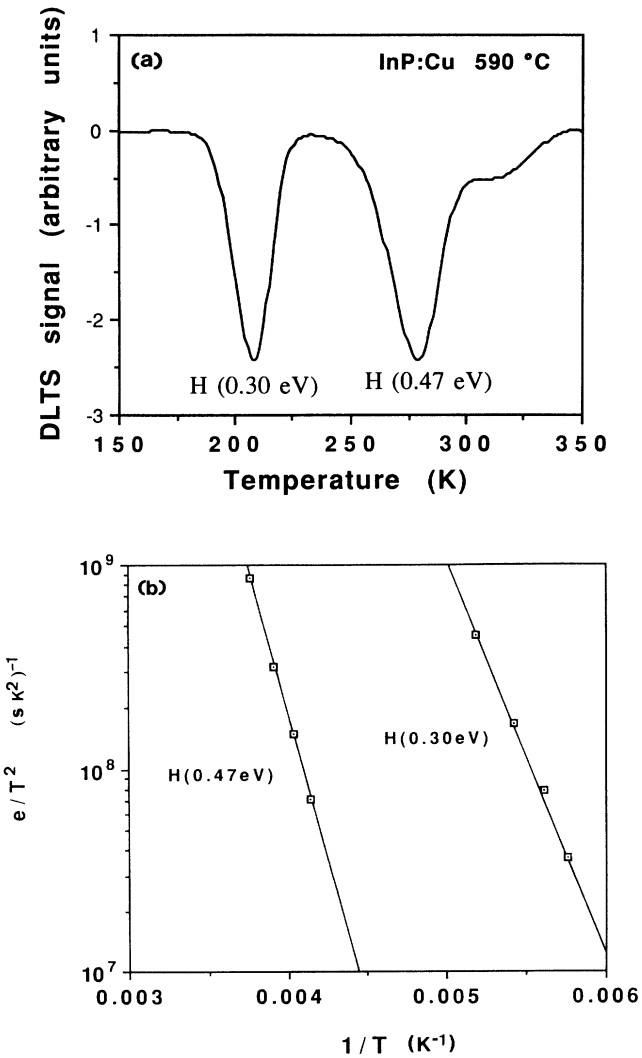

FIG. 7. (a) DLTS spectra showing the two hole traps found in p-InP:Cu. (b) Arrhenius plot corresponding to the spectra in (a). The energy levels were found to be $E_a=0.30$ and 0.47 eV, and both traps are found in concentrations of 1×10^{12} cm^{-3}.

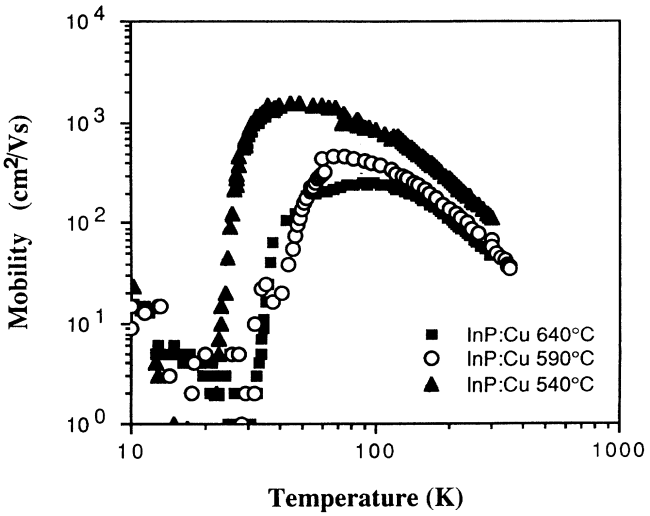

FIG. 9. Temperature dependence of the hole mobilities for p-InP:Cu samples with varying Cu concentration. The abrupt drop in mobility at low temperature is due to a transition to hopping conductivity.

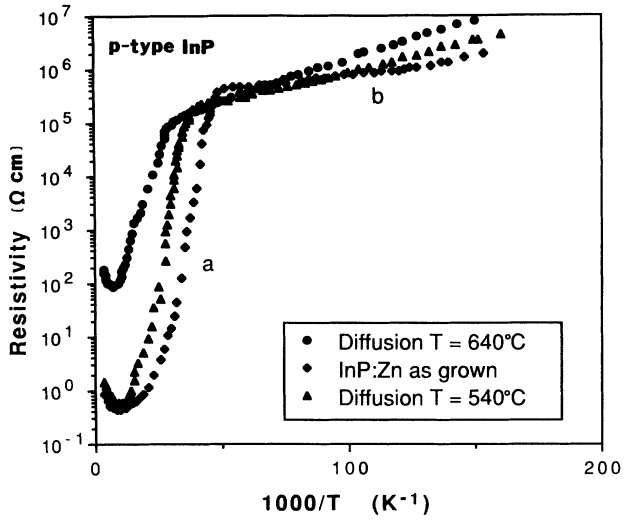

FIG. 10. Resistivity as a function of inverse temperature for two of the p-InP:Cu samples with a reduced carrier concentration (shown in Fig. 6) and the control p-InP:Zn sample with hole concentration of 4.5×10^{16} cm^{-3}.

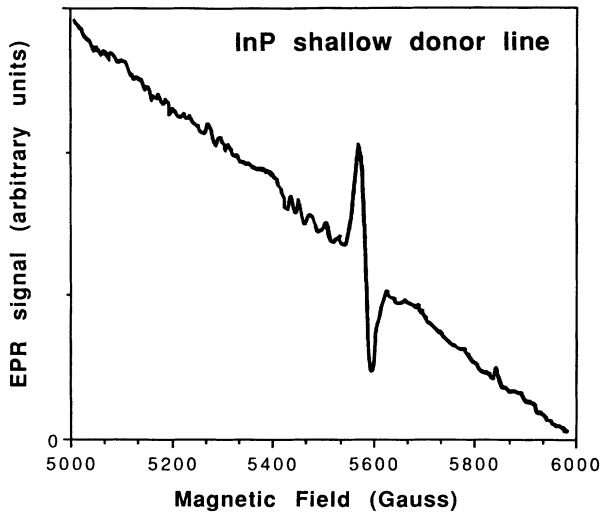

FIG. 12. EPR spectra from an InP:Cu sample that showed semi-insulating behavior when standard resistivity measurements were done. The peak shown in this plot between 5581 and 5606 G is characteristic of shallow donors in InP.

nitrogen temperature dropped from 18 000 cm^2/V sec in the untreated control sample to 750 cm^2/V sec for a sample diffused at 650 °C. All samples diffused above 550 °C showed a noticeable drop in both electron and hole mobilities. Figures 8 and 9 show the temperature dependence of electron and hole mobilities after different temperature diffusions. When the diffusion temperature was sufficiently high to cause InP:Cu to become semi-insulating, the room-temperature mobility recovered to approximately two-thirds of the original value in the as-grown samples.

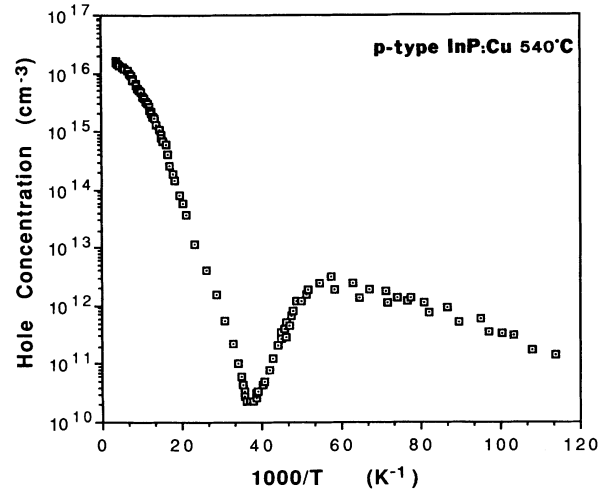

FIG. 11. Arrhenius plot of one of the p-InP:Cu samples. The apparent increase in carrier concentration in this plot occurs when both band-to-band and hopping conductivity are equivalent in magnitude. Such an increase is very typical of a transition to hopping conduction.

Figure 10 shows a plot of resistivity as a function of $1/T$ for two p-InP:Cu samples that were low in carrier concentration but not quite semi-insulating and also the as-grown p-InP control sample previous to the introduction of Cu. The most unusual and at first disconcerting feature of the plot in Fig. 10 is that the transition to hopping conductivity occurs at higher temperatures for p-type InP:Cu samples with lower carrier concentration.

Figure 11 shows an Arrhenius plot of the hole concentration for one of the samples. The temperature interval for which Hall measurements give an increase in carrier concentration occurs when both mechanisms of conductivity (band to band and hopping) are of equivalent magnitudes.

Figure 12 shows an EPR plot for an InP:Cu sample that was determined to be semi-insulating from electrical measurements. In seemingly contradictory fashion, this EPR plot shows the characteristic shallow donor peak for InP, indicating that part of the sample does not "freeze out" and is still highly conductive.

IV. DISCUSSION

The high solubility of Cu and its precipitation behavior could best be explained if we postulate that Cu has a high interstitial solubility at high temperatures. The measured high diffusivity of Cu in InP supports this statement. Upon cooling, the crystal is supersaturated with Cu that can be mobile as isolated interstitials even at room temperature. This supersaturation of Cu allows the formation of precipitates even with rapid quenching. Therefore, the behavior of Cu in InP appears to be very similar to Cu in Si.[17] On the other hand, it is well known that electrically active transition metals occupy substitutional sites in III-V semiconductors.[18] This allows the conclusion that the substitutional solubility of Cu in InP is

very low, considering the near absence of electrically active centers. This observation is supported by the channeling data showing that most of the Cu present in the InP lattice after diffusion forms precipitates.

The most straightforward explanation for the reduction in carrier concentration for both *n*- and *p*-type samples would be the introduction of both midgap hole and electron traps. These traps would have to be present in large enough concentrations so that compensation of shallow impurities in the prediffused samples could be possible. The results from the DLTS measurements clearly show that neither electron nor hole traps are responsible for InP's semi-insulating behavior after Cu diffusion. Hole traps of energies E_a equal to 0.30 and 0.47 eV were created in concentrations of 1×10^{12}, but this low concentration cannot explain a reduction in carrier concentration by 5×10^{15} cm^{-3} that is observed in the *n*-type InP:Cu samples that have an equivalent concentration of Cu. It is possible, however, that since these hole traps are found in similar concentrations, they correspond to substitutional Cu_{In}, and that this acts as a double acceptor similar to what it is found in both GaAs (Ref. 19) and possibly GaP.[20] The facts that the two peaks have a very close signal intensity and that their energy levels roughly correspond to what would be expected comparing the energy levels with the Cu_{Ga} double acceptor in GaAs using the empirical semiconductor band "line-up"[21] support this claim. The small concentration at which these traps were found, though, makes their unambiguous identification difficult. The temperature range at which DLTS measurements were performed was sufficient to observe the well-characterized 0.65-eV Fe level in InP,[22,23] but such a peak was not observed in our samples. This seems reasonable, considering the low diffusion temperatures (540 and 590 °C) used for the DLTS samples. The diffusivity and solubility of Fe in InP are extremely low at these temperatures,[24] and since a few micrometers were always cleaned from the surface of the samples to ensure complete removal of any undiffused metallic Cu, it is highly unlikely that unintentionally diffused Fe plays a significant role in the large apparent compensation in InP:Cu. DLTS results thus show that deep-level defects are not present in large enough concentrations to explain the large change in electrical properties observed after Cu diffusion in InP.

The Introduction outlines a recently proposed alternative explanation for the semi-insulating behavior of GaAs in which internal metallic precipitates act as buried Schottky barriers. This mechanism may be the best explanation available for the observed behavior of InP:Cu, and it may be applicable to similar systems such as GaP:Cu. The high total solubility of Cu in InP and its precipitation behavior are part of the conditions necessary for getting SI behavior with the buried Schottky-barrier mechanism. Estimates of the precipitate density, taking into account the sizes of the precipitates, the total Cu concentration, the expected barrier heights in InP and the initial carrier concentration show that there are enough Cu-In precipitates to cause depletion in the entire volume of the samples even at the relatively low diffusion temperature of 700 °C.

The extremely low mobilities resulting from the diffusion of Cu cannot be explained with scattering by ionized impurities, since a concentration of 10^{20} cm^{-3} ionized impurities would be necessary to explain the observed reduction in mobility. In our samples (see Figs. 8 and 9) carrier scattering is possibly dominated by the electric field from the space-charge regions, which could have an extremely large scattering cross section when compared with the scattering cross section for ionized impurities. The effect of metallic clusters on carrier mobility in semiconductors has been described theoretically by McNichols and Berg,[25] who also showed good experimental agreement in fast neutron irradiated GaAs. Their observation of a significant mobility decrease when about one-tenth of the sample volume is occupied by metallic inclusions with the associated depletion volumes is also consistent with our observations. The mobility component due to scattering of electrons from space-charge regions can be expressed as[25]

$$\frac{1}{\mu_s}=(2m^*kT)^{1/2}\frac{N_2\pi r_{\rm eff}^2}{q} ,$$

where m^* is the electron effective mass, q the electronic charge, N_s the concentration of metallic inclusions, and $r_{\rm eff}$ the effective scattering radius for electrons by the space-charge regions surrounding the precipitates. The expression for hole mobility scattering is analogous. This expression fits the mobility data obtained from Hall measurements in InP:Cu. This mobility component can also be expressed as a function of the differences in Fermi energy between the metal ($E_{\rm fm}$) and semiconductors ($E_{\rm fs}$). The dependence in this case is $1/\mu_s\sim(E_{\rm fs}-E_{\rm fm})^{2/3}$. In our observations this dependence is seen at least qualitatively, since when InP:Cu becomes semi-insulating, the room-temperature mobilities seem to partially recover to what they were in the original undoped samples before any Cu was introduced. In semi-insulating samples there is enough space-charge-region overlap to significantly "flatten out" ($E_{\rm fs}-E_{\rm fm}$), reducing significantly the electrostatic potential difference responsible for scattering from space-charge regions.

Hopping conduction can occur in compensated semiconductors near the Mott transition. The conductivity dependence on temperature in such semiconductors can be expressed as[26]

$$\sigma=\rho_1^{-1}e^{(\varepsilon_1/kT)}+\rho_3^{-1}e^{(\varepsilon_3/kT)} ,$$

where

$$\rho_3=\rho_0 e^{f(N_A)},\quad f(N_A)=\frac{\alpha}{N_A^{1/3}a} ,$$

and where σ is the total conductivity, ρ_i are the resistivities, ε_i are the activation energies, a is the atomic localization parameter (roughly equivalent to the Bohr radius for a shallow acceptor), and α is a constant. The first term represents the contribution from "band-to-band" conduction, and the second term the contribution due to hopping conduction. Figure 10 shows clearly the two types of conduction mechanisms, depicted as regions *a*

and b. It is apparent that there is a change in slope in resistivity versus $1/T$ and that the hopping mechanism of conduction becomes the most important conduction mechanism (region b) at lower temperatures. Other characteristics of hopping conductivity such as low mobilities and an apparent increase in the Hall measured carrier concentration as a function of $1/T$ were also observed in all p-InP:Cu samples. The exponential dependence of the term ρ_3 is due to the fact that the probability of a jump of a hole (or electron) i from an acceptor at point j is proportional to the square of the modulus of the overlap integral of the wave functions of the ground state of a hole (electron) at each of the acceptors (donors). At low acceptor (donor) concentrations the average distance between acceptors is $N_A^{-1/3} \gg a$, and therefore the probability of a jump between neighboring acceptors is exponentially small and the resistivity ρ_3 is exponentially large. Our control sample (p-InP doped with zinc) shows hopping at temperatures below 25 K. This type of conduction has been observed in other p-InP samples, so the expected transition temperatures and atomic localization parameters for shallow acceptors in InP are known.[27]

The occurrence of hopping conduction in samples with very small carrier concentrations is very unusual, since, given such low carrier concentrations (4×10^{14} cm^{-3} at room temperature for one of the samples), this would require a very large atomic localization parameter for overlap to occur and for hopping to be possible.[26] The atomic localization parameter can be extracted from the intercept of the resistivity plot. In one of the samples it was estimated that a would have to be almost 50 nm, which is over ten times larger than the published value of this parameter for the observed hopping conduction of Zn acceptors in InP.[27] Therefore, we conclude that the best explanation for the occurrence of hopping at such low shallow acceptor concentrations is nonuniformity in the concentration of carriers. In other words, hopping could only happen if there are pockets of conductive material intermixed with regions that have very low carrier concentration. If the low-resistivity regions were still connected, a percolation path could exist. This explanation is very compatible with the conditions necessary for the buried Schottky-barrier mechanism to apply, since there would be such a case of connected high-conductivity regions when the concentration of Cu in the samples is not high enough to form enough Cu-In precipitates to cause the entire sample to be depleted.

Whereas the previous argument can explain the occurrence of hopping at low carrier concentrations, it does not explain the transition to hopping conduction at higher temperatures for samples diffused with Cu. Instead, one has to remember that since the mobilities are much lower in InP:Cu than in as-grown material, the band-to-band component of the total conductivity is reduced, which makes the hopping component of the conductivity the most important conduction mechanism even at higher temperatures.

The data obtained from EPR studies confirm the model of nonuniformity in conductivity. Several samples that were semi-insulating when measured with Hall measurements showed the characteristic shallow donor peak between 5581 and 5605 G when measured at liquid-helium temperatures in the EPR cavity, indicating that portions of the material did not "freeze out" and were still highly conductive. However, a continuous current path no longer exists in these samples, so they appear semi-insulating when electrical measurements are performed on them. Figure 12 shows an EPR scan of a sample that appeared semi-insulating when its resistivity and carrier concentration was measured (Hall effect).

It could be argued that one feature of these results that the buried Schottky-barrier model does not explain is the closeness between the values for the electron and hole activation energies when InP becomes semi-insulating. If Schottky barriers are responsible for the intrinsic behavior of this material, one might expect an activation energy closer to what the known barrier heights are with metals deposited *in situ* on InP cleaved in ultrahigh vacuum. This would give values of 0.32–0.54 eV for n-InP (Ref. 28) and 0.76–0.98 eV for p-InP.[29] However, the conditions for contact formation are not the same, since it is well known that semiconductor surfaces have a great influence in ultimate barrier heights, and surface interactions are not present with an internal metal semiconductor contact. There are also significant differences in between deposition of a metal on a semiconductor surface and the nucleation and growth of a metallic precipitate.

V. SUMMARY AND CONCLUSIONS

In summary, the experiments described herein show many observations: (i) Cu has a large total solubility and a large diffusivity in InP. (ii) InP becomes semi-insulating after Cu diffusion at temperatures of 700 °C and above. (iii) Both initially p-type and n-type samples undergo this semi-insulating transition. (iv) There are negligible deep level defects introduced by Cu. (v) Most of the Cu forms Cu-In precipitates. (vi) The mobility of both electrons and holes reduces abnormally as a result of Cu diffusion. (vii) The InP:Cu samples are very inhomogeneous in their electrical behavior.

The concurrence of these observations can best be explained by the buried Schottky-barrier model, and none of these are inconsistent with it. Therefore, one can conclude that this mechanism could have general applicability and important technological promise not only to provide an alternative to Fe doping in obtaining semi-insulating InP, but also to make any semiconductor material intrinsic as long as a large enough concentration of precipitates of a metallic phase is achievable.

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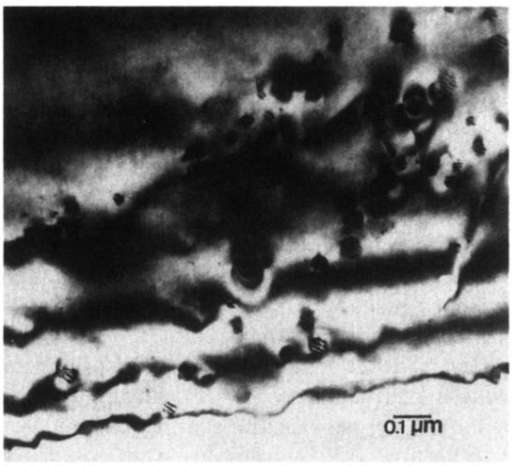

FIG. 3. Plan view TEM micrograph (two beam condition, bright field) of an InP:Cu sample that was diffused at 950 °C. Samples diffused at lower temperatures also contain precipitates, but of smaller diameters. The Cu-rich precipitates showing Moire fringes can be clearly seen here.