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Deep levels in hafnium- and zirconium-doped indium phosphide

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4*d* and 5*d* transition metals Zr and Hf were introduced into *n*-type InP using low-pressure–metal-organic chemical-vapor deposition up to the concentration of $(1-3)\times 10^{17}$ cm^{-3}. The epilayers were investigated by deep-level transient spectroscopy with a view of searching for the deep levels associated with substitutional Hf and Zr, which are isovalent to Ti, a midgap deep donor in InP. In InP:Hf, three deep levels could be associated with Hf. Detailed emission rate, concentration profile, and capture cross-section measurements were undertaken for these three levels, Hf*A*, Hf*B*, and Hf*C*, which were found to have energy positions $E_c-0.51$ eV, $E_c-0.15$ eV and $E_c-0.12$ eV, respectively. Hf*A* was found to be a good candidate for the level associated with the isolated substitutional Hf in InP. The InP:Zr samples revealed two levels Zr1 and Zr2, with energy positions $E_c-0.53$ eV and $E_c-0.10$ eV, respectively, Zr1 being possibly the level due to the substitutional Zr.

I. INTRODUCTION

Although doping with transition metals is the only reliable way of obtaining high-resistivity InP-based materials needed for the fabrication of high-speed optoelectronic devices, the physics of the electronic properties of transition metals in III-V semiconductors remains far from well understood. A few transition-metal impurities are known to introduce deep levels near the middle of the band gap of III-V semiconductors, which can compensate for shallow donors or acceptors, resulting in a semi-insulating material. The search for deep levels caused by transition-metal impurities in III-V semiconductors has been an active area of investigation, motivated mainly by this technological implication. One finds a lack of systematic investigations of the electrical properties of transition metals in III-V semiconductors in the literature.

In InP, only 3*d* transition metals have been researched extensively hitherto. Among these, Fe (Ref. 1) and Ti (Ref. 2) give rise to deep levels suitable for obtaining semi-insulating properties. In the case of Fe, a deep acceptor in InP, device applications are often limited by its low thermal stability.[3,4] Ti, on the other hand, acts as a deep donor level in InP and is thermally much more stable than Fe.[4] 4*d* and 5*d* transition metals are expected, in general, to be much more thermally stable due to their larger atomic sizes.[5] It has recently been shown[6] that the 4*d* element Zr and 5*d* element Hf are indeed thermally very stable in InP. Thus there is considerable interest in the electronic properties of 4*d* and 5*d* transition metals in InP, about which very little is known presently. To the best of our knowledge only one report, by Bremond *et al.*,[5] has appeared in literature about the electrical characterization of 4*d* transition metals in InP. They have tried to search for deep levels resulting from a number of 4*d* transition metals in InP, without finding any level which could be associated with a particular transition metal they tried. However, they did not try Zr. The present paper aims at the investigation of possible deep levels caused by isovalent series of the group-IV transition metals Ti(3*d*), Zr(4*d*), and Hf(5*d*).

We have investigated Hf- and Zr-doped InP in search of deep levels arising from the presence of these transition metals. The doping is achieved by low-pressure–metal-organic chemical-vapor deposition (LP-MOCVD), which is the state-of-the-art technique for growing InP epilayers for optoelectric device fabrication. Deep-level transient spectroscopy (DLTS) is employed for the characterization of deep levels. The results of doping with Hf are presented here while the preliminary results of Zr doping have been reported earlier.[6]

II. EXPERIMENT

For LP-MOCVD growth, trimethylindium and phosphine were used as In and P sources, respectively. The precursor used for Hf doping was dimethylhafnocene $(CH_3)_2Hf(C_5H_5)_2$ while the Zr source was dimethylzircocene $(CH_3)_2Zr(C_5H_5)_2$. Both precursors were kept at 10 °C during growth. The pressure inside the bubbler was adjusted to 200 mbar for dimethylzircocene and 1000 mbar for dimethylhafnocene. The growth temperature was 640 °C. All layers were grown at a rate of 2.7 μm/h, with a nominal thickness of 2.7 μm.

Two kinds of Hf-doped InP epilayers were grown. For one kind, semi-insulating InP:Fe substrates were used. The dimethylhafnocene flow was varied from zero (reference sample) to 100 Ml/min. For the second kind, n^+-InP substrates were used and Si was codoped along with Hf at a doping level of 5×10^{16} cm^{-3}. Again the dimethylhafnocene flow was varied. The Zr-doped layer was grown on an n^+-InP substrate. It was codoped with Si. The dimethylzircocene flow was 4 Ml/min.

For space-charge measurements, diodes were fabricated on the grown epilayers by successive evaporation of 5-nm Ni, 100-nm Zn, and 200-nm Au followed by a short heat treatment at 340 °C causing Zn to diffuse, resulting in a p^+n junction and top Ohmic contact. The diodes were circular in shape and 180 μm in diameter. The details of diode fabrication have been reported earlier.[7] For samples grown on n^+ substrates, the bottom Ohmic contact to the substrate was simply made by silver epoxy, which also provided the mounting to the ground of ceramic chip carriers, which was placed in a cryostat for measurements. For samples grown on semi-insulating substrates, the lift-off technique was used for lateral integration of Ohmic contacts and diodes. First, the alloyed Ohmic contacts to the n-type LP-MOCVD layers were made by successive evaporation of 7-nm Ni, 100-nm, Au/Ge (88:12), and 150-nm Au followed by alloying at 400 °C. Then, with a second lift-off process, the diodes were fabricated.

The concentration of Hf and Zr in LP-MOCVD-grown layers was measured by secondary-ion-mass spectroscopy (SIMS). Hall-effect measurements on as-grown wafers and capacitance-voltage (*C-V*) measurements on fabricated diodes were used to measure the free-carrier concentration in the epilayers. Current-voltage (*I-V*) measurements, in conjunction with *C-V* measurements, were employed to check the quality of the diodes fabricated.

Deep-level investigations were conducted using the DLTS technique. Full isothermal capacitance transients over a range of temperature were recorded using a Boonton 7200 capacitance meter, the filling pulses being applied by an HP 8115A pulse generator. Standard DLTS or double-correlation (differential) DDLTS spectra were generated from the stored transients by boxcar analysis.

III. RESULTS

While the free-carrier concentration in the undoped LP-MOCVD InP epilayers was as low as 5×10^{14} cm^{-3} at 300 K, it was much higher in the Hf-doped epilayers, ranging from 7×10^{15} to 5×10^{16} cm^{-3}. It increased almost linearly with dimethylhafnocene carrier gas flow. In the InP epilayers codoped with Si, also, the free-electron concentration increasing with increased Hf incorporation from 5×10^{16} cm^{-3} in samples without Hf, up to 1×10^{17} cm^{-3} with maximum Hf concentration.

The SIMS measurements showed that Hf was present in our LP-MOCVD epilayers up to a concentration of 1×10^{17} cm^{-3}. Zr was incorporated at a level of 3×10^{17} cm^{-3} for both elements, ion-implanted standards were used to calculate concentrations from the SIMS data.

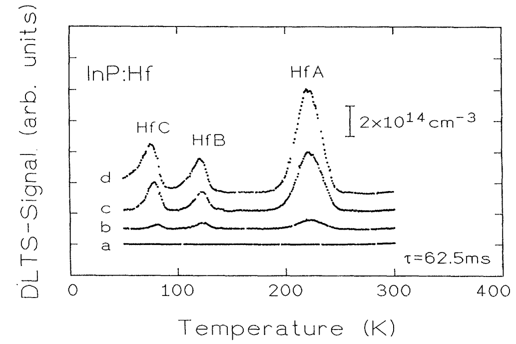

FIG. 1. DLTS spectra of an InP reference sample (curve *a*), compared with those of InP:Hf samples with (curve *b*) smallest, (curve *c*) larger, and (curve *d*) largest Hf concentrations (among the three). The base line on the vertical scale has been shifted for each spectrum for clarity.

DLTS measurements on a large number of Hf-doped and reference samples revealed a number of deep levels in these epilayers. Three of these deep levels were found to be present in all Hf-doped samples, and were not found in reference samples. These three levels (named Hf*A*, Hf*B*, and Hf*C*) can be seen in Fig. 1, which shows the DLTS spectra of three Hf-doped samples (*b*, *c*, *d*), along with that of a reference sample (*a*). Spectra *b*–*d* are for increasing dimethylhafnocene carrier gas flow during the LP-MOCVD growth. The emission rate signatures of Hf*A*, Hf*B*, and Hf*C* levels are depicted in Fig. 2. The best-fit lines to these data in this Arrhenius plot provide activation energies of 0.51, 0.24, 0.12 eV to the conduction-band edge, respectively, for the three levels. These activation energies, along with the electron-capture cross sections σ_∞ at $1/T=0$ obtained from the extrapolation of the Arrhenius plots of Fig. 2, are tabulated in Table I.

We have tried to measure the electron-capture cross sections σ_n of these levels directly by the usual varying-

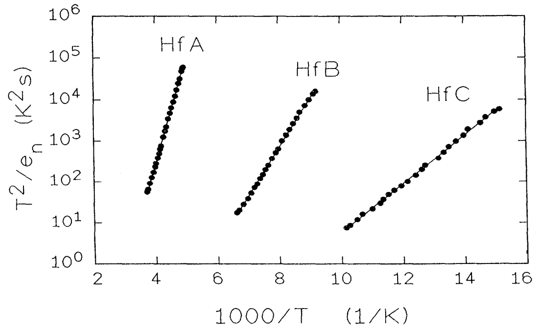

FIG. 2. Emission rate signatures of the three Hf-related deep levels in InP:Hf. Activation energies are $E_A=E_C-0.51$, $E_A=E_C-0.15$, and $E_A=E_C-0.12$ eV for Hf*A*, Hf*B*, and Hf*C* respectively.

TABLE I. Electrical characteristics of the Hf-related levels in InP.

Level	Activation energy (eV)	σ_∞ (cm^2)	σ_n (cm^2)	Capture barrier (E_B) (eV)	Energy position below c.b. (eV)
Hf*A*	0.51	2.9×10^{-13}	$>5.0\times10^{-18}$ (203–207 K)		
Hf*B*	0.24	2.0×10^{-14}	7.6×10^{-22} (122 K)	0.09	0.15
Hf*C*	0.12	5.6×10^{-16}	$>5.0\times10^{-18}$ (66–98 K)		

pulse filling method. It was found that the DLTS peak heights of the levels Hf*A* and Hf*C* did not reduce upon the application of the excitation pulse of the shortest width that was possible to use in our system (1 μs). This corresponds to $\sigma_n > 5\times10^{-18}$ cm^2 for these two levels. It was, however, possible to measure it for the Hf*B* level, and it was found to be $\sigma_n = 7.6\times10^{-22}$ cm^2 at 122 K. This capture cross section was temperature dependent, increasing with increase in temperature. Figure 3 shows this temperature dependence of σ_n. The slope of the best-fit straight line to the data points gives an energy of activation for the capture process $E_B = 93\pm10$ meV. Corrected for this barrier height for electron capture from the conduction band to the deep level, the actual energy position of the level Hf*B* is $E_c - 0.15$ eV.

The concentration depth profiles of the three levels were measured using DDLTS. All three levels Hf*A*, Hf*B*, and Hf*C* were found to be distributed uniformly within the space-charge region produced by these measurements. Figure 4 gives typical profiles showing that the deep-level concentrations did not exhibit variation with depth from the junction.

Comparing the concentrations of the deep levels Hf*A*, Hf*B*, and Hf*C*, resulting from Hf doping, with the concentration of the Hf atoms in the samples as measured from SIMS, the deep-level concentrations were found to be much smaller. Figure 5 shows this comparison for the three samples whose DLTS spectra were given in Fig. 1. As seen from the figure, although the deep-level concentrations are about two orders of magnitude smaller than the Hf atomic concentration, a certain correlation between the two concentrations can be seen. All three levels increase in concentration with increase in the Hf concentration in InP. This is particularly evident for the Hf*A* level, while Hf*B* and Hf*C* tend to saturate in concentration beyond a particular level, as the atomic concentration of Hf increases.

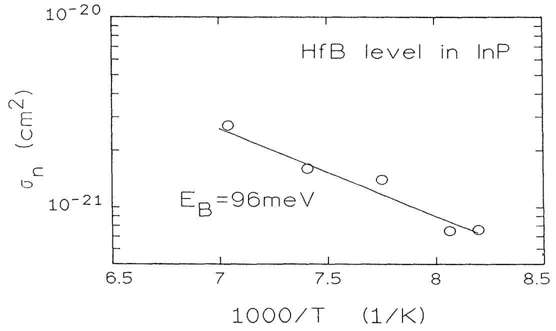

FIG. 3. The temperature dependence of electron-capture cross sections of the level Hf*B*.

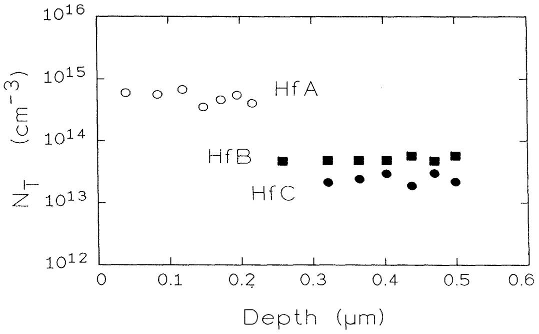

FIG. 4. Variation in Hf-related deep-level concentrations as a function of depth from the metallurgical junction. The profile of Hf*A* was measured in a sample having large donor concentration, so that the range of probed depths is smaller than that for Hf*B* and Hf*C* for which the measurements were carried out on a lower doped sample.

The Zr-doped InP epilayers revealed the presence of two deep levels, named Zr1 and Zr2, with electron activation energies 0.53 and 0.10 eV to the conduction band, respectively, which were not observed in the reference samples. This is depicted in Fig. 6, which shows the DLTS spectra of Zr-doped and reference samples. The strong peak around 130 K seen in the spectrum of InP:Zr belongs, most probably, to the Ni^+/Ni^{2+} level[8] that has sometimes been observed in our LP-MOCVD-grown InP layers, and can also be seen in the spectrum of the reference sample in this figure. Other unmarked smaller peaks could also be identified with previously reported deep levels in InP. Thus Zr1 and Zr2 are the two levels that are peculiar to the Zr-doped layers. Figure 7 shows their typical emission rate signatures. The concentrations of the two levels, in the range of $1-7\times10^{14}$ cm^{-3},

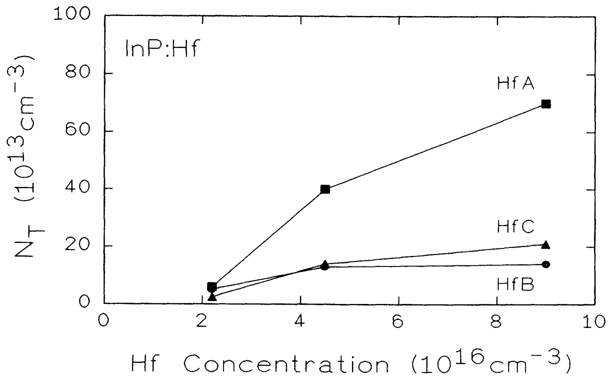

FIG. 5. The variation of the Hf-related deep-level concentration with the Hf atomic concentration in InP.

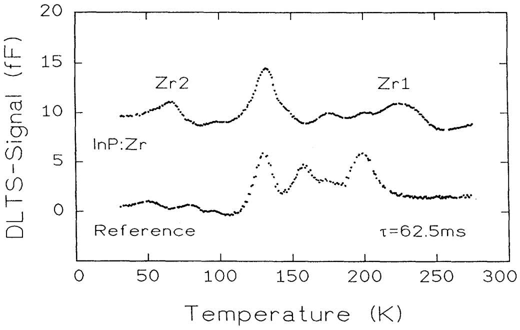

FIG. 6. DLTS spectra of Zr-doped and reference InP samples. The base line for the InP:Zr spectrum has been shifted on the vertical scale for clarity.

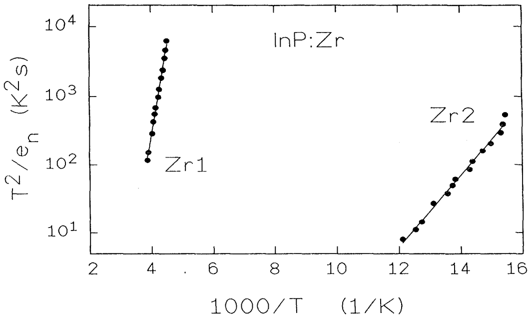

FIG. 7. Emission rate signatures of the Zr-related levels in InP. Activation energies are $E_A = E_C - 0.53$ and $E_C - 0.10$ eV for Zr1 and Zr2, respectively.

were again much smaller than the Zr atomic concentration in the epilayer, measured by SIMS, which was 3×10^{17} cm^{-3}.

IV. DISCUSSION

Since the three levels Hf*A*, Hf*B*, and Hf*C* were found in all Hf-doped samples and were not found in reference samples, they could be related to the presence of Hf in InP epilayers. The uniformity of spatial profiles of their concentrations also strengthens this possibility, showing that they are not associated with any technology-related point defects. However, their much smaller concentration compared with the Hf atomic concentration, as measured from SIMS, raises doubts about such an assignment. The definitive statement that can be given is that these levels result from the transition-metal precursor. However, since the precursor mainly results in the presence of Hf, the major candidate for the origin of these levels has to be Hf itself. The higher concentration of Hf*A*, and the consistent increase in it with the Hf concentration, makes this level the main contender for the isolated substitutional Hf in InP. Comparing with the SIMS results, this would mean that most of the Hf atoms either do not go to substitutional sites or that some other species, complexing with them, render them electrically inactive. It might be pointed out here that in InP, the concentration of the deep level due to the substitutional Rh (the RhA level[9]), another 4*d* transition metal, was also recently found to be about two orders of magnitude lower than the atomic Rh concentration. The large atomic sizes would tend to limit the solubility of these 4*d* and 5*d* elements, so that the probability of forming electrically inactive aggregates cannot be ruled out. The other two levels, Hf*B* and Hf*C*, could be complexes of Hf atoms with other impurities or structural defects.

In the case of Zr doping, the two levels Zr1 and Zr2 can be Zr related. Of these, the Zr1 level was also observed in samples implanted with Zr ions.[6] Thus it could be the level of the isolated substitutional Zr in InP. Here again, the deep-level concentration is much smaller than the Zr atomic concentration. The other level, Zr2, could be a complex involving Zr and another impurity/structural defect.

It might be noted that the emission rate signatures of the Hf*A* and Zr1 levels are similar, which means that not only are the energies of the two levels similar but also the electron-capture cross sections. This may not merely be a coincidence; it could have deeper physical significance. The two transition metals have similar ionization potentials in vacuum (Zr^{3+}: -33.6 eV, Hf^{3+}: -32.4 eV) as well as ionic radii (Zr^{3+}: 0.077 nm, Hf^{3+}: 0.085 nm).[10]

The 3*d* transition metal Ti (vacuum ionization potential -42.3 eV),[10] which is isovalent to Zr and Hf, gives rise to a substitutional deep donor in InP. The levels Hf*A* and Zr1 could, therefore, possibly be substitutional donors. This probable assignment is in agreement with the general trends in III-V semiconductors, expected from theoretical calculations.[11] According to these trends, going down a column of the Periodic Table, the depth of a transition-metal level from conduction band should decrease slightly. Since the Ti donor in InP lies at 0.59 eV below the conduction band,[2] Zr at 0.53 eV and Hf at 0.51 eV would follow this trend.

V. CONCLUSIONS

With an aim of investigating the electronic properties of the isovalent series Ti(3*d*), Zr(4*d*), and Hf(5*d*), InP was doped successfully with transition metals Zr and Hf. DLTS measurements revealed three levels which could be related to the presence of Hf in InP:Hf. The concentrations of the centers responsible for these levels are $<10^{15}$ cm^{-3}. Of these, level Hf*A*, with energy position $E_c - 0.51$ eV, was found to be a good candidate for the level resulting from isolated substitutional Hf in InP. In the Zr-doped InP samples, two levels could be related to the presence of Zr, with level Zr1, at $E_c - 0.53$ eV, being possibly due to the isolated substitutional Zr.

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