Oxygen-based deep levels in metalorganic vapor phase epitaxy indium gallium arsenide

J. W. Huang and T. F. Kuech[a)]
Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706

T. J. Anderson
Department of Chemical Engineering, University of Florida, Gainesville, Florida 32611

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We have studied the defect engineering in metalorganic vapor phase epitaxy $In_xGa_{1-x}As$ by controlled oxygen doping. Diethylaluminum ethoxide (DEALO) was used as an oxygen precursor to provide the intentional deep level incorporation. DEALO doping in $In_xGa_{1-x}As$:Si with $x \leqslant 0.25$ resulted in the reduction in carrier concentrations. The Al and O incorporation with a DEALO mole fraction was weakly dependent on alloy composition for $x \leqslant 0.25$. The degree of electrical compensation, however, decreased as the In content increased at the same oxygen content. Deep level transient spectroscopy investigations on a series of $In_xGa_{1-x}As$:Si:O samples with x ranging from 0 to 0.18 reveal a set of oxygen-derived deep levels, similar to those found in DEALO-doped GaAs. These characteristic deep levels appear to remain at a relatively constant energy with respect to the valence band, as compared to the rapid decrease in the conduction band of $In_xGa_{1-x}As$ with x. © *1995 American Institute of Physics.*

Semi-insulating (SI) $In_{0.53}Ga_{0.47}As$ would be useful for 1.5 μm range photodetectors and device isolation in high speed signal processing. Nominally undoped epitaxial $In_{0.53}Ga_{0.47}As$ typically contains a net free electron concentration in excess of 1×10^{15} cm^{-3}.[1] Transition metal doping has been used to incorporate deep level impurities for the compensation of net shallow impurities.[1–3] Transition elements generally exhibit a high thermal diffusion coefficient and can migrate during annealing when used in ion-implanted device structures. These deep level trap densities may also be limited by the transition metal solubility limit.[3] Recently, intentional oxygen incorporation into metalorganic vapor phase epitaxy (MOVPE) GaAs with alkoxide precursors has been developed.[4,5] The oxygen-related multiple deep levels within the GaAs band gap result in the compensation of shallow Si donors,[5] and the major deep electron traps were determined to be ~0.75 and ~0.95 eV below the conduction band minimum (E_c).[6]

We have extended the use of diethylaluminum ethoxide [DEALO, $(C_2H_5)_2AlOC_2H_5$][5] to In0.53Ga0.47As layers. Initial studies found that $In_{0.53}Ga_{0.47}As$:O was not semi-insulating. The situation here seems to be similar to the case of $In_{0.53}Ga_{0.47}As$:Cr, where electron concentration increases with Cr doping level.[2] To fully investigate this effect, we have systematically grown a series of $In_xGa_{1-x}As$:Si:O samples with x at 0, 0.06, 0.12, 0.18, and 0.25 in order to follow the variation of the electrical properties and deep level structures. Similar studies were performed to investigate the intrinsic EL2 defect in nominally undoped $In_xGa_{1-x}As$ grown by the $AsCl_3$ vapor phase epitaxy process,[7] MOVPE,[8] and molecular beam epitaxy.[9] The ability to manipulate the deep level impurity incorporation via DEALO doping in the MOVPE process would provide us with a direct route for identifying the role of oxygen and its effects on the properties of $In_xGa_{1-x}As$, as well as other compound semiconductors.

This letter presents the study of electrical characteristics of MOVPE $In_xGa_{1-x}As$ $(0 \leqslant x \leqslant 0.25)$ with intentional oxygen incorporation. All samples were grown in a conventional horizontal low pressure (78 Torr) MOVPE reactor[5] using trimethyl gallium (TMGa), trimethyl indium (TMIn), and arsine (AsH_3) on Si-doped n^+ (100) GaAs substrates with 2° off toward (110). Disilane (Si_2H_6) was employed for n-type Si doping, and DEALO for oxygen incorporation. The growth temperature was 600 °C and the V/III ratio (AsH_3/TMGa) was 40 to 60. A typical growth rate was 0.035 μm/min. A step graded buffer layer was grown first before the thick $In_xGa_{1-x}As$ layer (1 μm or more) to allow the growth of low dislocation density $In_xGa_{1-x}As$ epilayers on GaAs. The growth details will be presented elsewhere.[10] The actual In composition of the top thick $In_xGa_{1-x}As$ layers was determined by carrying out electron probe microanalysis.

The EC–V profiling characterization was performed on multilayer $In_xGa_{1-x}As$:Si:O samples. These samples were grown on top of the underlying grading layers and with a growth sequence in which only the DEALO mole fraction was varied in a stepwise fashion. The growth temperature, V/III ratio, and Si_2H_6 mole fraction were kept constant throughout. Additional single layer (~1 μm thick) $In_xGa_{1-x}As$:Si:O samples were also grown on top of the grading layers for DLTS measurements. Even with these grading layers, the possibilities of misfit dislocation-induced deep level states[11] acting as traps and affecting DLTS spectra cannot be completely ruled out. Therefore, complementary single layer $In_xGa_{1-x}As$:Si growths without DEALO were performed as control samples. Au Schottky contacts were deposited using a standard lithography and liftoff process. Conventional DLTS scans were performed using double box-car correlators.[6]

The use of a step graded buffer layer has led to cross-

[a)]Electronic mail: kuech@engr.wisc.edu

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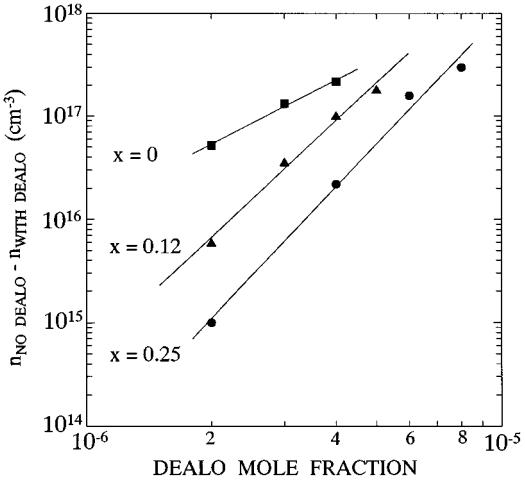

FIG. 1. Free carrier concentration reduction as a function of DEALO mole fraction at different x in $In_xGa_{1-x}As$:Si:O Free carrier concentrations of $In_xGa_{1-x}As$:Si without oxygen doping are 3.9×10^{17}, 3.0×10^{17}, and 3.8×10^{17} cm^{-3} for $x=0.25$, 0.12, and 0, respectively.

hatching surface morphology, characteristic of dislocation formation, on all our $In_xGa_{1-x}As$ samples with smooth areas between the cross-hatching lines. The multilayer samples of $In_xGa_{1-x}As$:Si:O were grown and studied with x at 0.25, 0.12, and 0. Si_2H_6 mole fractions in these three samples were adjusted so that free carrier densities of the top $In_xGa_{1-x}As$:Si layers were all $3-4\times10^{17}$ cm^{-3}. Free carrie concentration reduction ($\Delta n = n_{\text{no oxygen}} - n_{\text{with oxygen}}$) was observed in all three samples by EC–V profiling. A higher DEALO mole fraction was required to produce similar reduction, as illustrated in Fig. 1, when x was increased. We have performed secondary ion mass spectroscopy analysis on these three samples. Al and O contents were both found to be only weakly dependent on In composition.[12] The change in the degree of compensation with In composition can therefore be attributed to the variation in the depth and concentration of the oxygen-related deep levels.

We have performed DLTS analysis on the series of single layer $In_xGa_{1-x}As$:Si:O samples for x equal to 0, 0.06, 0.12, and 0.18. Along with the series of nonoxygen-doped $In_xGa_{1-x}As$:Si samples, EC–V free carrier densities of both sets of samples are shown in Table I, labeled as ''Si/O'' and ''Si only,'' respectively. No DLTS peak was detected over the temperature range of scan (77–410 K) in the ''Si only'' control samples, indicating that the effects of dislocation or strain induced deep levels on the DLTS spectra are not significant in non-DEALO-doped $In_xGa_{1-x}As$. The intrinsic EL2 defect with an expected concentration $\leqslant 1.5\times10^{14}$ cm^{-3} (Ref. 8) is beyond our DLTS detection limit at this doping level. Features in DLTS spectra of $In_xGa_{1-x}As$:Si:O can thus be attributed exclusively to DEALO doping. Activation energies were obtained through the standard Arrhenius plots.[6] Assuming negligible capture barrier heights, these activation energies are taken to be the energy differences between E_c and deep levels. All DLTS spectra in Fig. 2 were adjusted to produce comparable DLTS signal levels. The factors of adjustment, as labeled in Fig. 2

TABLE I. $In_xGa_{1-x}As$ DLTS samples from Fig. 2. N_d-N_a were determined by EC–V measurements and in the unit of 1×10^{17} cm^{-3}.

x	N_d-N_a (Si only)	DEALO mole fraction ($\times10^{-6}$)	N_d-N_a (Si/O)	$\Delta(N_d-N_a)$
(a) 0	1.0	0.75	0.6	0.4
(b) 0.06	3.5	3	2.0	1.5
(c) 0.12	3.0	5	0.5	2.5
(d) 0.12	3.0	4	1.8	1.2
(e) 0.18	4.1	5	2.4	1.7

and reflecting the difference in deep level concentrations, are found to be consistent with the differences in $\Delta(N_d-N_a)$ as shown in Table I.

The DLTS spectrum of $x=0$ [Fig. 2(a)] is the same as previously reported,[6] with major deep levels at $E_c-0.73$ (No. 2) and 0.93 (No. 1) eV along with some other minor levels at $E_c-0.53$ (No. 3) and 0.31 eV. Similar multiple oxygen-related deep levels were also found to be present at $x=0.06$, as shown in spectrum (b1) of Fig. 2 with a major peak No. 2 at $E_c-0.66$ eV and two other shoulder peaks (No. 3 at $E_c-0.48$ eV, and No. 1, of which the exact energy level is not resolved). A comparison between spectra (a) and (b1) indicates that, as the band gap was decreased upon alloying with In, the general shape of the DLTS spectrum was essentially unchanged with No. 2 remaining as the major peak, but the emission energies (to E_c) of all deep levels were reduced. A similar trend was also observed in Fig. 2 when x was increased to 0.12 (peak No. 2 and No. 3 at $E_c-0.60$ and 0.46 eV) and 0.18 (peak No. 2 and No. 3 at $E_c-0.54$ and 0.41 eV). The effect of oxygen doping level on deep level structure is also illustrated in Fig. 2, where the

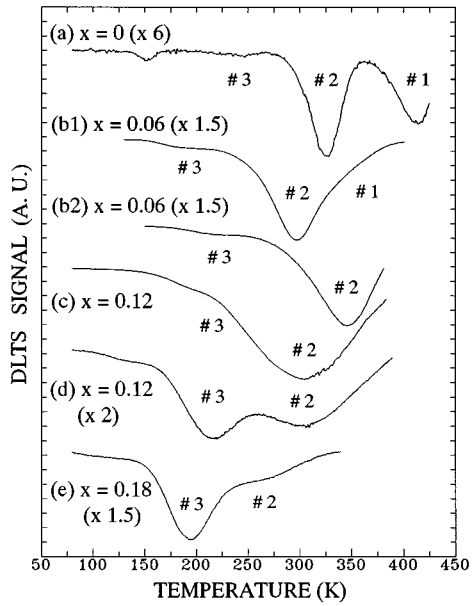

FIG. 2. DLTS spectra of $In_xGa_{1-x}As$:Si:O with x=(a) 0, (b1) 0.06, (b2) 0.06, (c) 0.12, (d) 0.12, and (e) 0.18. Measurement conditions for (a) and (b1) are as follows: reverse bias -1 V, pulse height 1 V, pulse width 0.1 ms, pulse period 500 ms, rate window 11.6 s^{-1}. Measurement conditions for (b2), (c), (d), and (e) are as follows: reverse bias -0.5 V, pulse height 0.5 V, pulse width 0.1 ms, pulse period 20 ms, rate window 1162.8 s^{-1}.

DEALO mole fraction was varied in two otherwise identical $x=0.12$ samples [(c) and (d) in Table I]. Two major peaks No. 2 and No. 3, exhibit a shift in relative peak heights, and this shift is directly related to the change in DEALO doping level. This observation is very similar to the GaAs:Si:O case where the height of peak No. 2 would be reduced relative to peak No. 1 of Fig. 2(a) at lower DEALO mole fraction.[6] The DLTS spectral comparison of $x=0.12$ and $x=0.18$ indicates that peak No. 3 dominated over peak No. 2 at $x=0.18$.

We have previously attributed the observed multiple peaks in DEALO-doped GaAs and the shift in relative peak heights to the variations in charge states or local defect atomic configurations, specifically the number of Al nearest neighbors to the oxygen.[6] A recent study[13] on intentional oxygen doping of GaAs using dimethylaluminum methoxide has reported similar DLTS spectra as in Fig. 2(a), and assigned peak No. 3 as an isolated off-center substitutional oxygen (Ga–O–Ga). The major traps, peaks No. 2 and No. 1, were attributed to complexes of Al and O involving two and one Al atoms, respectively. The weaker In–O bond (86 kcal/mole), when compared to the Al–O (121.3 kcal/mole) or Ga–O (91 kcal/mole),[14] would indicate that the oxygen-related defect should still be dominated by the local configuration of Al–O bonds as in the case of GaAs. We have therefore assumed that the same set of defect configurations are responsible for the observed DLTS spectra for $x=0$ to 0.18, similar to the case of the EL2 defect in undoped $In_xGa_{1-x}As$,[7–9] and labeled the corresponding peaks in Fig. 2 accordingly. The peak height distribution in Fig. 2 is shifted from that found in GaAs:O with increasing In content and DEALO mole fraction. While the overall features of the spectra are the same, this change in peak heights indicates that there are substantive changes in the atomic level incorporation of oxygen at the growth front. The detailed mechanism of attachment of oxygen at the growth front, most probably dominated by processes at step edges,[15] is not understood but will determine the local configuration of the incorporated oxygen.

There is only little valence band (E_v) offset at the $In_xGa_{1-x}As/GaAs$ heterojunction.[16] The measured deep level evolution of $In_xGa_{1-x}As:Si:O$, as x is increased, is depicted in Fig. 3 relative to a constant E_v. Since there is little shift in E_v with composition, this diagram is therefore referenced to the vacuum level.[16] The deep levels No. 2 and No. 3 appear to remain relatively constant with respect to E_v, in contrast to the rapid decrease in E_c of $In_xGa_{1-x}As$ with x.[17] This relative invariance of the deep level energy relative to E_v is similar to the case of the intrinsic EL2 defect in $In_xGa_{1-x}As$[7–9] in spite of their different microscopic origins, and could have resulted in the reduced compensation in $In_xGa_{1-x}As$ $(0\leqslant x\leqslant 0.25)$ with larger x and the high electron concentration in $In_{0.53}Ga_{0.47}As$, as one or more of these deep levels become resonant with E_c. Many transition metal impurity deep levels, referenced to a common level (such as the vacuum level), are known to be invariant to the specific host semiconductor, while other defects tend to follow a specific band edge.[18,19]

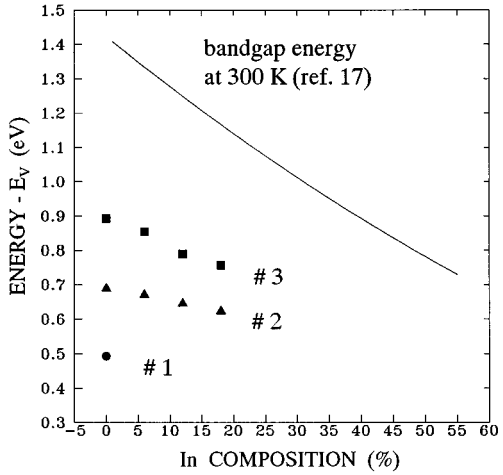

FIG. 3. Deep level structure evolution of $In_xGa_{1-x}As:Si:O$ based on DLTS results.

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