Defect characterization in GaAlInAs alloys

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Deep level transient spectroscopy (DLTS) and capacitance-voltage measurements at various temperatures have been used to characterize defects in Si-doped $(Ga_{1-x}Al_x)_{1-y}In_yAs$ materials for $x=0.3$ and different values of y (0, 0.005, and 0.07). We only detect DX centers, those associated with the doping impurity (Si), but also others associated with Te and, eventually, Sn not introduced intentionally. When the experimental conditions are chosen to obtain exponential transients, the shape of the DLTS spectrum and its variation with the filling pulse duration can be accounted for by this contamination; i.e., no sign of the so-called alloying effect is detected.

I. INTRODUCTION

GaAlAs alloys contain a defect, called DX center,[1] directly related to the presence of the n-type doping impurity, which introduces spurious effects in electrical as well as optical devices. Its electronic properties have been extensively studied (for a detailed description see Ref. 2). For this reason, various means have been attempted to suppress this defect. Kobayashi et al.[3] reported the reduction of DX centers in GaAlAs alloys, in which In has been introduced, for particular alloy compositions. Typically, the concentration of the DX center in $(Ga_{1-x}Al_x)_{1-y}In_yAs$ with $y=0.05$ is found to be one order of magnitude lower in a $x=0.3$ material, but larger in a $x=0.5$ material, than in the corresponding alloys for $y=0$. The authors attribute this observation to a band-structural effect, stating without further justification that the DX concentration should decrease near the Γ, L crossover (around $x\simeq0.4$ in GaAlAs alloys), which is shifted near $x=0.3$ when In ($y=0.05$) is added. This result is discussed by Pann et al.[4] who argue that the change in the DX concentration is only apparent, i.e., related to the electron occupancy of the defect as a consequence of the variation of DX energy level relative to the bottom of the conduction band. In addition, Pann et al.[4] observed a structure in the deep level transient spectroscopy (DLTS) spectrum for particular values of y. They conclude that the DX characteristics are sensitive to their local atomic configuration (the so-called alloying effect). The aim of this work is to study this question quantitatively, using DLTS, by measuring the DX energy level and the barrier associated with electron capture, in both In-doped and undoped alloys. It is also to investigate more closely the question of the so-called alloy disorder effect induced by In.

II. SAMPLES AND TECHNIQUE

The layers used in this study were grown by molecular beam epitaxy (MBE) on an n^+-doped GaAs substrate.

They are Si doped at a concentration N_D of the order of 10^{16}–10^{17} cm^{-3}, as measured by capacitance-voltage (C-V) measurements (see Fig. 1). Their Al content is identical ($x=0.30$), while y varies from 0 (sample a: $N_{Da}=9\times10^{16}$ cm^{-3}) to 0.005 (sample b: $N_{Db}=4\times10^{16}$ cm^{-3}) and 0.07 (sample c: $N_{Dc}=10^{18}$ cm^{-3}).

Gold Schottky barriers are deposited on the surface to allow capacitance measurements (C-V) and DLTS while ohmic contacts are prepared on the substrate. As is well-known, the DLTS spectrum associated with the DX center is strongly distorted for a number of reasons, originating from physical characteristics of this defect as well as from experimental conditions under which it is recorded.[5,6] In order to study quantitatively electron emission from this center, it is necessary to fulfill a number of conditions.[6] The main one consists of filling only a small fraction of the center, i.e., to use very short filling pulses t_p. Indeed, in this case, only a small fraction of DX centers are filled, which insures that neither the capture rate nor the capture barrier (which depends on band filling) vary during capture[7] since the free electron concentration (difference between the doping concentration and the concentration of filled DX centers) can then be considered to be constant. We therefore used the smallest t_p values compatible with the sensitivity of the experiment, namely 1–50 μs. However, the amplitude ΔV of the filling pulse that is used is not small enough to avoid the enhancement of electron emission by the electric field.[8–10] Consequently, in order to compare spectra obtained for two different materials, we used experimental conditions such that the electric field in the space-charge region is the same in both cases.

III. RESULTS

A. GaAlAs material

A typical DLTS spectrum of a sample not doped with In (sample a) is shown in Fig. 2. It contains three peaks at 130 (P1), 160 (P2), and 210 K (P3) for an emission rate $e_n=60$ s^{-1} in the temperature range studied (80–300 K). These peaks correspond to DX centers associated with dif-
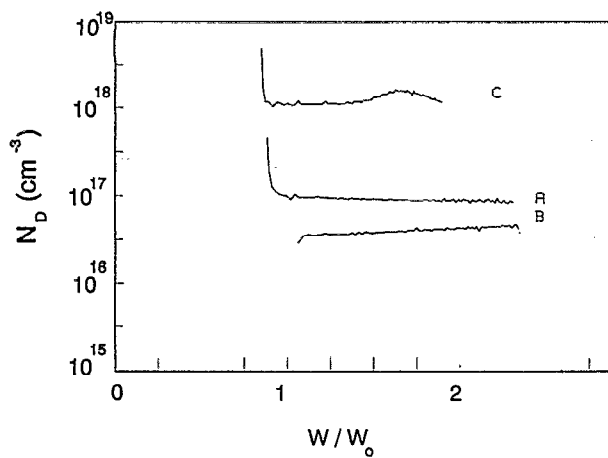
FIG. 1. Free electron concentration at room temperature vs depth W in the various alloys (a) $y=0$, (b) 0.005, and (c) 0.07 as deduced from capacitance-voltage measurements. W_0 is the width of the space charge region for 0 V bias [(a)0.07 μm; (b)0.14 μm; (c)0.019 μm].

FIG. 3. Variation of the emission rate e_n vs temperature for the peaks P1 ($\bigcirc$), P2 ($\square$), and P3 ($\triangle$) (see Fig. 2) observed in samples a and b obtained using the experimental conditions of Fig. 2. The signatures for the DX centers associated with Si, Te, and Sn (full lines) obtained in samples intentionally doped with these impurities are also given.

ferent impurities: the Si doping impurity at 210 K and residual impurities; Te at 160 K and Sn at 130 K. This can be demonstrated by comparing the signatures (variation of e_n vs T^{-1}) of these three peaks with the signatures obtained in materials intentionally doped with Si, Te, and Sn impurities (Fig. 3). The Si-doped samples ($x=0.30$) were MBE grown, the Te-doped ones ($x=0.25$) were light emitting diodes grown by liquid phase epitaxy (LPE), and the Sn-doped ones ($x=0.33$) were grown by metalorganic chemical vapor deposition (MCVD). They were selected for these alloy compositions as close as possible from the x value of the samples studied in this work. The doping concentrations, in the range 10^{16}–10^{17} cm^{-3}, were chosen so that the same physical situation could be applied in the DLTS measurements. The relative amplitudes of these three peaks do not give the relative concentrations of the Si, Te, and Sn impurities because they are not filled with
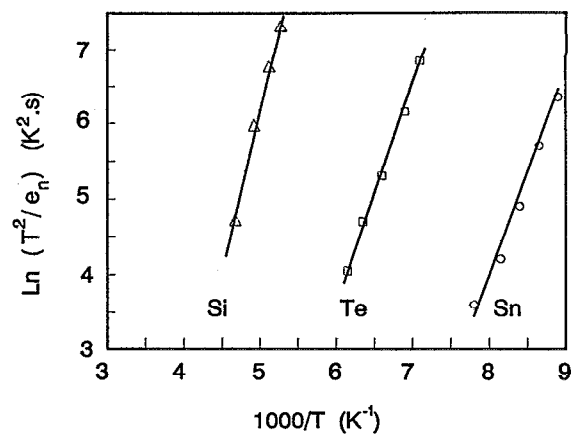
the same rates. Indeed, the corresponding DX centers do not have the same values for the capture barrier. This can be easily illustrated by varying the filling duration, which results in a change in the relative amplitudes of the peaks. In Fig. 4, for instance, the DLTS spectrum contains the same P1, P2, and P3 peaks as in Fig. 2 for $t_p=20$ μs exhibiting amplitudes increasing from P1 to P3. However, the DLTS spectrum for $t_p=10$ ms contains only the P3 peak and a fraction of the P2 peak having both similar amplitude. This is due to the fact that the capture barrier is higher for the Si DX center than for the Te DX center. As a result, the Te DX center is filled for shorter t_p values than the Si DX center (this will be detailed in the next section). Actually, the P2 amplitude is even larger than the P3 one because the P2 spectrum is truncated in the low-temperature range (what is observed is only the high-
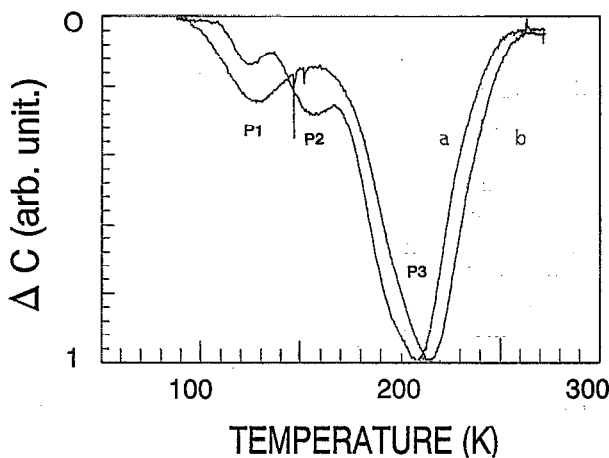

FIG. 2. DLTS spectra obtained for samples a and b. The reverse voltage is $V_0=-1$ V, the pulse amplitude $\Delta V=0.9$ V, the filling pulse duration $t_p=50$ μs, and the emission rate $e_n=60$ s^{-1}.
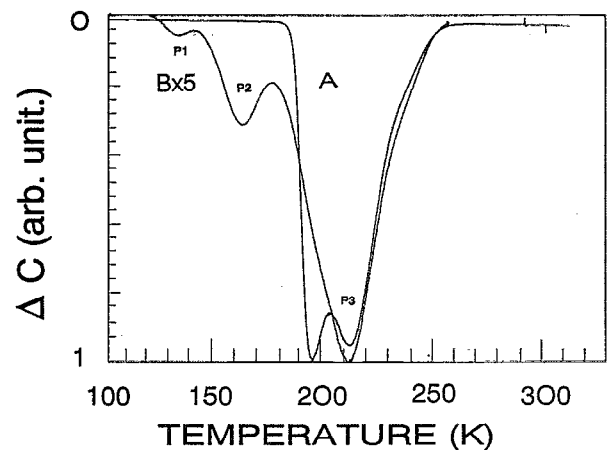

FIG. 4. DLTS spectra in the $y=0$ material (sample a). The experimental conditions (emission rate 21 s^{-1}) are identical except for the filling pulse duration, which is 20 μs (spectrum B, amplitude multiplied by 5) and 10 ms (spectrum A), respectively. (Peak 2 appears at a slightly lower temperature than in Fig. 2 because the emission rate is slower.)
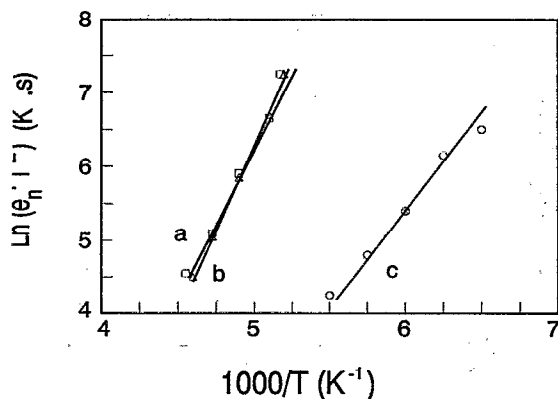
FIG. 5. Variation of the emission rate vs temperature for the peak P1 observed in samples a, b, and c obtained using the experimental conditions of Fig. 2.

FIG. 7. DLTS spectrum observed in sample c (emission rate 60 s^{-1}, $V_0=-1$ V, $\Delta V=0.9$ V) for different values of t_p: 50 μs (1), 10 μs (2), and 1 μs (3).

temperature side of the peak), due to the strong drop in the filling factor below 160 K (this filling factor varies abruptly with temperature for a given filling time, as explained in Ref. 6).

We measured the concentration of the Si associated DX centers (P3 component) filled with a filling duration of 50 μs; it is $C_a=9.5\times10^{14}$ cm^{-3}. The P3 associated ionization energy is $E_{ia}=425$ meV and the barrier $B_a=220$ meV; quantities deduced respectively from the variations versus the inverse of the temperature of the emission rate (Fig. 5) and of the logarithm of the quantity $-T^{1/2}\,e_n[1-(\Delta C_m/C_0)]$ (Ref. 11) where ΔC_m is the peak amplitude and ΔC_0 the peak amplitude corresponding to completely filled centers (Fig. 6). These values agree correctly with the values already published for these quantities.[5]

B. In-doped materials

The DLTS spectrum of the $y=0.005$ In-doped material (sample b) obtained using the same experimental conditions as for sample a, is also given in Fig. 2. This spectrum is similar to the spectrum of sample a but has a higher P1 amplitude and a lower P2 one. This indicates
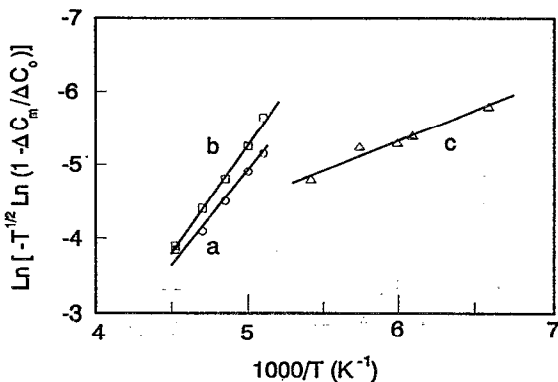

FIG. 6. Variation of the logarithm of $-T^{1/2}\ln[1-(\Delta C_m/\Delta C_0)]$ vs temperature obtained for samples a, b, and c under the same conditions as in Fig. 2.
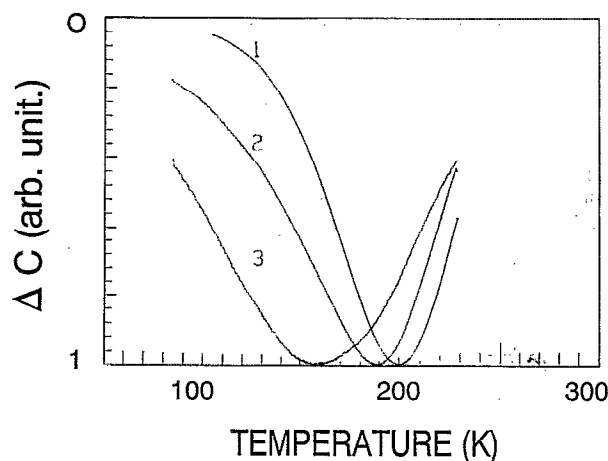
that this material is less contaminated by Te but more by Sn than the material not In doped. The values of the ionization energy and capture barrier of peak P3 are, respectively, $E_{ib}=430$ meV, $B_b=250$ meV (see Figs. 5 and 6, respectively). The amplitude of the P3 peak for $t_p=50$ μs corresponds to a concentration of filled DX centers equal to $C_b=3.8\times10^{13}$ cm^{-3}.

As to sample c, In doped with $y=0.07$, its DLTS spectrum is considerably wider and slightly shifted to lower temperatures (see Fig. 7). For a filling rate of 50 μs, the corresponding ionization energies and barriers are (see Figs. 5 and 6, respectively): $E_{ic}=285$ meV and $B_c=33$ meV. The peak amplitude corresponds to a filled DX concentration $C_c=8.1\times10^{15}$ cm^{-3}. For these samples, the temperature of the peak and the width of the spectrum depend strongly on the filling duration t_p. As illustrated in Fig. 7, when one uses shorter filling pulses, the width of the spectrum increases and the peak temperature shifts toward lower values. The corresponding values of the ionization energies and capture barriers also vary accordingly as shown in Figs. 8 and 9. The reason for this behavior is the presence of the residual donor impurity (Te), which gives rise to a DX peak at a lower temperature (the peak P2 at 160 K) than the Si one that peaks around 200 K (component P3 in Fig. 2). This second component P2 is not clearly seen as in the case of Fig. 2. Because the capture barrier for the Te DX centers is smaller than for Si DX centers (the difference is about 200 meV [11] whatever the alloy composition x), the spectrum is dominated by the Si component P3 for large t_p values because their concentration is considerably larger. However, for low t_p values, the fraction of filled Si DX centers is small owing to the large value of the capture barrier and the spectrum contains two components P2 and P3 associated with both the Si and Te DX centers. The resulting spectrum is wider and thus shifts apparently to lower temperatures as a result of the relative variations of these two components. Consequently, the measured ionization energies and capture barriers are a
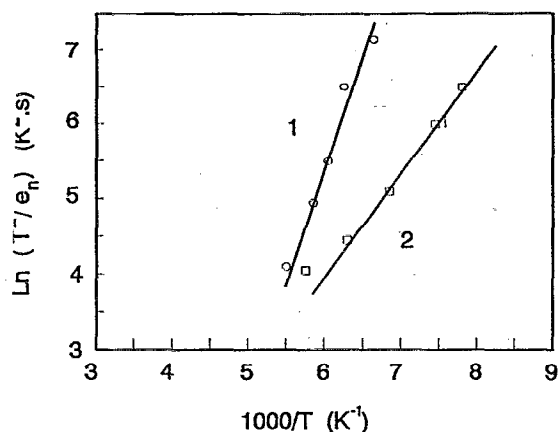
FIG. 8. Variation of the emission rate e_n vs temperature for the peak observed in sample c obtained under experimental conditions of Fig. 2 for $t_p = 50$ μs (1) and 1 μs (2).

strong function of t_p and have no physical meaning in this case.

Thus, the fact that the DX spectra obtained with $t_p = 50$ μs are wider for sample c than for samples a and b, and shifted to lower temperatures, has to be ascribed to the existence of a relatively large residual Te contamination (which is estimated to be ~10^{16} cm^{-3}, the detection limit, by secondary ion mass spectroscopy). This is not surprising since Te-doped samples were also grown in the system. The observed change in B and E_i vs y cannot be attributed to the presence of In, but to the existence of this large Te contamination. However, because for $t_p = 50$ μs, the P3 (Si) component dominates largely over the P2 (Te) one, the measured concentration C_c represents a reasonable evaluation of the filled Si DX centers.

V. DISCUSSION

We first examine the possible change in the DX concentration induced by In doping. For this we consider only the DX centers associated with Si (peak P3). In order to compare the concentrations of DX centers in two different
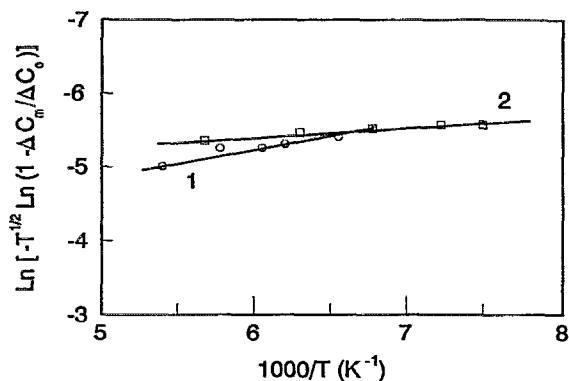

FIG. 9. Variation of the logarithm of $-T^{1/2} \ln[1 - (\Delta C_m/\Delta C_0)]$ vs temperature in sample c obtained in the same conditions as in Fig. 7: $t_p = 50$ μs (1) and 1 μs (2).

materials, one has to take into account the variation of the filling factor with the donor concentration N_D. The filling rate is $C_n n$, where n is the free electron concentration and C_n the thermally activated capture rate [12]

$$C_n = \sigma_0 v_n \exp\left(\frac{B}{kT}\right)$$

(v_n is the electron thermal velocity). During the capture process, n varies as $N_D - C(t)$, where $C(t)$ is the filled DX concentration at a given time t. However, for small filling times t_p, such that $C(t_p)$ remains very small compared to N_D, the filling factor is simply proportional to $C_n n$, where n is equal to N_D. Then the concentration of filled centers for a given t_p value varies from one material i containing N_{Di} donors to another j containing N_{Dj} donors, as

$$\frac{C_j}{C_i} = \frac{N_{Dj}}{N_{Di}} \exp\left(\frac{(B_i - B_j)}{kT}\right),$$

assuming that σ_0 does not vary with the composition x of the material, a reasonable assumption, since the DX center possesses intrinsic properties defined by its local atomic and electronic structure, i.e., independently of x.

Then the concentration of DX centers that should be filled (for $t_p = 50$ μs) in sample b, if this sample had the same donor concentration and the same capture barrier as sample a, is $C_b' = 3$–6×10^{14} cm^{-3}, owing to the accuracy of measurements on the barriers B, to be compared to $C_a = 9.5 \times 10^{14}$ cm^{-3}. Thus, it appears that In doping even at the level of $y = 0.005$ has decreased the concentration of DX centers.

The above formula assumes that all the DX centers are ionized at the peak temperature T_p. Actually, the ionized fraction depends on the energetic location of the DX level: $E_{DX} = E_i - B$ below the bottom of the conduction band. Since the introduction of In decreases E_{DX} (from 205 meV for $y = 0$ to 180 meV for $y = 0.005$), one has to introduce a corresponding correction factor $\exp(-\Delta E/kT_p)$, i.e., 3–5 in this case, which means that $C_b' \sim 1$–2×10^{15} cm^{-3}, i.e., is of the order of C_a. The decrease of the DX concentration with In doping is thus the result of the variation of E_{DX} vs y. We therefore conclude, in agreement with the conclusion of Pann et al.,[4] that this decrease is directly related to the filling fraction of the DX level with the change of band structure.

The same analysis for sample c, in the same conditions (i.e., for $t_p = 50$ μs) cannot be made since the barrier is not determined correctly in this case. The concentration of DX centers expected if sample c had the same donor concentration as sample a is $C_c' = 1.1 \times 10^{15}$ cm^{-3}, i.e., is identical to C_a within the experimental accuracy if we assume no change in the capture barrier. However, this barrier must be larger since even a smaller value of y has increased it significantly. Therefore, the introduction of In at a level of 7% must diminish the DX concentration but the extent of the change cannot be estimated correctly.

We now turn toward the question discussed at length by Pann et al.[3] on the physical meaning of the peaks exhibited by the DLTS spectrum. These authors attribute the

existence of these peaks to a variation in the ionization energy of DX centers versus the nature (In or Al) of second neighbor atoms of the Si impurity. As in the case presented here, they observe a DLTS peak whose maximum shifts in temperature as t_p varies when two components are clearly revealed (one peak around 160 K and the other around 200 K). But we have shown here that the temperatures of these peaks are the temperatures expected for the DX spectra associated respectively with Te and Si. We therefore argue that the behavior of the DLTS spectrum they observe should be understood in terms of a contamination with Te (or eventually Se) and perhaps Sn impurities and not in terms of an alloying effect. This is clearly demonstrated by the fact that one of the components (which they label DXC) exhibits an ionization energy having exactly the ionization energy of the Te associated DX center.

The alloying effect postulates that the DX center is a deep defect whose characteristics (wave function, energy level, and capture cross section) are sensitive to the local environment, i.e., to the presence of Al atoms located in its neighborhood.

The existence of this effect was first proposed[13] to account for the large distribution of capture time constants in Si-doped materials. This distribution was fitted using a Gaussian distribution of barriers said to originate from the alloying effect (Actually, a Gaussian distribution is hardly compatible with the existence of only four possible environments corresponding to the four components observed in the DLTS spectrum.) The quantitative analysis of the data which has been made[14] demonstrates that the activation energies associated with all the components is (within ±10 meV, i.e., the experimental accuracy) constant that implies that both the energy level E_T and the barrier B associated with the capture cross section do not depend on the atomic environment of the defect thus contradicting the initial postulate.

Baba et al.[15,16] also observed a multicomponent DX spectrum in Si-doped GaAs that is periodically doped by a monolayer of AlAs. These components were ascribed to DX centers having different Al environments, as in the case of Ref. 14. The ionization energies of these components varies from 295 meV, for Si said to be surrounded by only Ga atoms, down to 175 meV when Al atoms are in second nearest neighbor position. Hence, in this case there is a large shift in the ionization energy of the DX center with its environment. This result therefore contradicts the analysis presented in Ref. 14. The existence of multiple components in simple disordered GaAlAs layers and in selectively doped ordered alloys must therefore have a different origin since they have different electronic characteristics.

In the case of disordered alloys, our study shows that the effect of contamination with residual donor impurities has to be taken into account in the spectrum analysis. When this is done no alloying effect is then detected.

In conclusion, the observations of several components in the DX DLTS spectrum of In-doped materials should not be understood in terms of an alloying effect but to an effect of contamination with nonintentionally introduced donor impurities.

ACKNOWLEDGMENT

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