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Dissociation kinetics of the *EL*2-hydrogen complex in passivated GaAs

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Hydrogen passivates shallow dopants as well as the *EL*2 defect in *n*-type GaAs. The passivation of the *EL*2 defect is shown to be thermally less stable than the shallow dopant passivation. Thermal dissociation of the *EL*2-H complex under an applied reverse bias occurs more rapidly than under zero-bias conditions. It is shown that the reverse bias dissociation is characterized by two first-order processes, one considerably more rapid than the other. The rapid process has an activation energy of 1.33 eV and a dissociation attempt frequency of $1.0\times10^{14}\mathrm{s}^{-1}$.

Exposure of GaAs to a hydrogen plasma is known to passivate shallow dopants and to render some defects deep in the band gap electrically inactive.[1] The *EL*2 defect in particular has been shown to be passivated by hydrogen.[2] The passivation has been reported by Omel'yanovski, Pakhomov, and Polykov[3] to be more stable than that of the shallow dopants with only 10% reactivation after 30 min annealing at 623 K. Cho *et al.*[4] reported regeneration of the defect's electrical activity after 10 s rapid thermal annealing at 830 K.

In this paper we show that the *EL*2 is significantly less stable to annealing than previously reported. Our measurements indicate that the thermal dissociation of the *EL*2-H complex is characterized by two processes which are first order over the range of annealing times used. We report the dissociation kinetics of the *EL*2-H complex and further show that the dissociation rate is affected by the application of an electric field during the annealing.

The GaAs used in this work was grown at 670 °C by atmospheric pressure metallorganic vapor phase epitaxy on Si-doped ($n = 1\times10^{18}$ cm^{-3}) substrates. Samples with free carrier densities of $n = 2\times10^{16}$ cm^{-3} (Si doped) and $n = 1\times10^{16}$ cm^{-3} (S doped) were used. After Ni-AuGe-Ni Ohmic contacts had been formed on the back of the substrates, the samples were exposed to hydrogen plasma for 1 h at 180 °C in a parallel plate system similar to that described in Ref. 5. The hydrogen pressure was 0.4 mbar, and the sample was mounted on a heater block about 10 cm downstream from the plasma. After passivation, the sample was lightly etched to remove 0.2 μm of the material so as to prevent any surface damage created by the plasma treatment from affecting the electrical measurements. Gold Schottky contacts were evaporated onto the Si-doped samples. Because of their superior thermal stability,[6,7] ruthenium Schottky contacts were fabricated on the S-doped samples which were used for the kinetic measurements. Ohmic and Schottky contacts were also evaporated onto reference samples which had not been exposed to the plasma. Capacitance-voltage (*C*-*V*) profiling at 1 MHz showed hydrogen penetration to a depth of 0.7 μm in the passivated material.

Deep level transient spectroscopy (DLTS) measurements carried out on a digital system[8] showed that the *EL*2 trap was passivated by exposure to the hydrogen plasma. The *EL*2 concentration in a sample annealed for 30 min at 400 K typically recovered 25% of its original concentration. *C*-*V* measurements on passivated samples before and after annealing showed negligible change in the shallow dopant concentration. It may therefore be accepted that any changes observed in DLTS peak heights are not related to reactivation of shallow dopants. It should be noted that the annealing temperatures used are considerably lower than those previously reported[3] and that the *EL*2 passivation is clearly less stable than that of the shallow donors.

Measurement of the dissociation kinetics of the *EL*2-H complex requires knowledge of the *EL*2 concentration prior to passivation. This concentration was measured in a reference sample. In order to compare the *EL*2 concentration in a given reference and passivated sample, the reverse bias and pulse height in the reference sample were adjusted so that the same spatial depth was sampled for both samples. The different free carrier densities in passivated and reference samples were also taken into account.

A S-doped sample was passivated and then subjected to annealing under 2 V reverse bias at 366 K. The *EL*2 peak height is plotted as a function of annealing time in Fig. 1. The data were collected at the peak temperature of the chosen DLTS rate window and annealing was carried out at the same temperature.[9] It is apparent that there is a more rapid initial reactivation over the first approximately 10^5 s after which the recovery of the *EL*2 proceeds more slowly. The concentration of the passivated *EL*2 defect or *EL*2-H complex may be derived from these data since

$$[EL2\text{-H}] = [EL2]_{\mathrm{total}} - [EL2], \tag{1}$$

where [*EL*2-H] is the concentration of the *EL*2-H complex in the passivated sample, [*EL*2] is the electrically active *EL*2 concentration in the passivated sample, and the total *EL*2 concentration $[EL2]_{\mathrm{total}}$ is measured in the reference sample.

A first-order dissociation process for the *EL*2-H complex is characterized by the equation

$$N(t) = N_0 \exp[-\nu(T)\, t], \tag{2}$$

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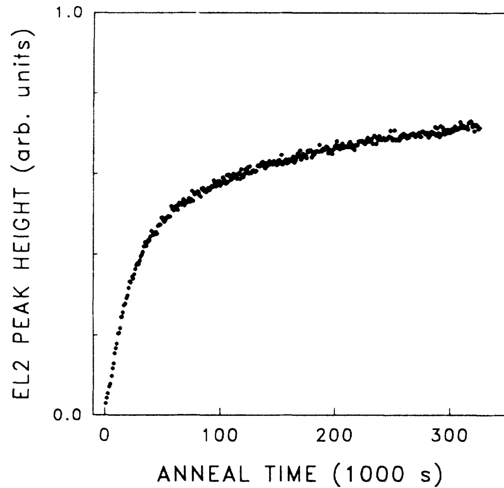

FIG. 1. $EL2$ peak height in passivated S-doped GaAs as a function of annealing time at 366 K.

where $N(t)$ is the time-varying complex concentration, N_0 the concentration of the complex on commencement of annealing, and $\nu(T)$ the dissociation rate at the specific annealing temperature. A plot of the natural logarithm of the concentration against anneal time is linear for a first-order reaction. We shall show that the dissociation of the $EL2$-H complex may be characterized by two first-order processes, one significantly faster than the other. This implies two components to the $EL2$-H concentration, one which decays rapidly which we shall denote N_1 and a slowly decaying component denoted N_2. The total time-varying $EL2$-H concentration may be written as

$$N(t) = N_{10}\exp[-\nu_1(T)\,t] + N_{20}\exp[-\nu_2(T)\,t], \tag{3}$$

where N_{10} and N_{20} are the initial concentrations of the two components and ν_1 and ν_2 the respective reaction rates.

Figure 2 shows the natural logarithm of the complex concentration plotted against annealing time. The solid line is a fit to data for annealing times greater than 2×10^5 s at which stage the rapid reaction appears to have run to completion. The linearity of this portion of the curve indicates that the slow reaction is first order. With ν_2 and N_{20} determined from this fit, the contribution of the slow decay was subtracted from the experimental data for the shorter annealing times. The resulting data representing the rapid reactivation process are plotted logarithmically in Fig. 3. The linearity again indicates a first-order process. The reaction rates for the fast and slow processes at 366 K were determined to be $\nu_1 = 3.5\times10^{-5}$ s^{-1} and $\nu_2 = 1.6\times10^{-7}$ s^{-1}, respectively.

The $EL2$ is believed by some to be a family of related defects[10,11] rather than a single level. The two observed reactivation rates could be explained in terms of two slightly different $EL2$ components in our samples which interact differently with hydrogen. The trap energy (0.82 eV) and capture cross section (1×10^{-13}cm^{-3}) of the reactivated $EL2$ were measured by DLTS. These parameters are not significantly different from those measured for the $EL2$ in the reference samples. We therefore conclude that if two $EL2$ components exist their trap signatures do not differ significantly. An alternative and more probable explanation is that there are two configurations of the $EL2$-H complex with the hydrogen occupying different sites in each case.

Similar annealing experiments were carried out at a variety of temperatures. The annealing kinetics of the $EL2$-H complex may be determined from the relationship

$$\nu(T) = \nu_0 \ \exp[-\ E_a \ / \ kt], \tag{4}$$

where E_a is an activation energy for the rapid dissociation and ν_0 is the dissociation attempt frequency. The reactivation rates for the rapid process are plotted on the Arrhenius plot shown in Fig. 4. A dissociation attempt frequency ν_0 of $1.0\times10^{14\pm1}$ s^{-1} and an activation energy of 1.33 ± 0.05 eV for the dissociation of the $EL2$-H complex were determined. The attempt frequency falls within the range expected for GaAs.[12] The activation energy for the reactivation of passivated shallow dopants

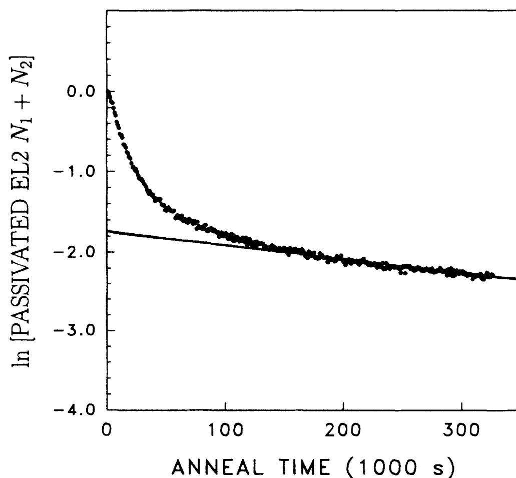

FIG. 2. Natural logarithm of the $EL2$-H complex concentration as a function of annealing time at 366 K. Sample: passivated S-doped GaAs. The fitted line indicates the slow (N_2) component of the $EL2$ reactivation.

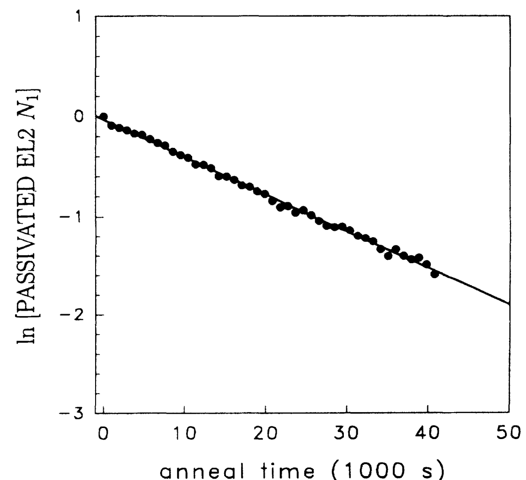

FIG. 3. Natural logarithm of the rapidly decaying $EL2$-H component N_1 after subtraction of the slow component N_2.

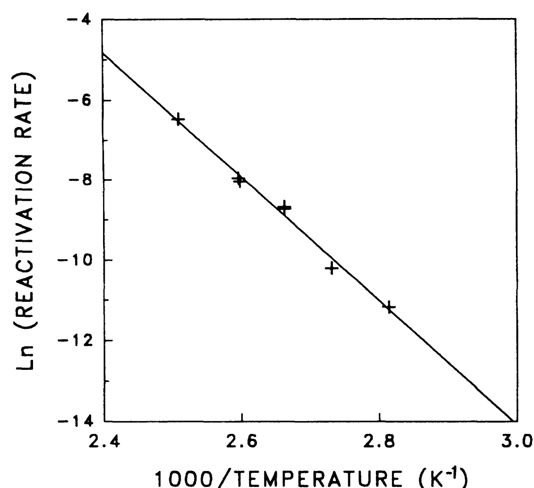

FIG. 4. Arrhenius graph for the rapid reactivation of the $EL2$ in S-doped GaAs.

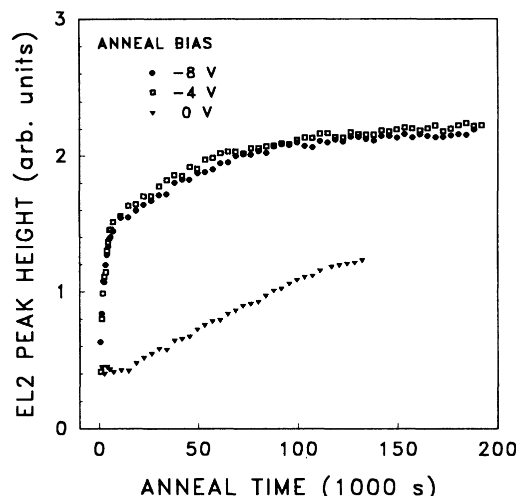

FIG. 5. $EL2$ peak height in S-doped GaAs as a function of annealing time at 386 K under zero bias, and reverse bias of 4 V and 8 V.

when annealed under reverse bias is reported to be of the order of 1.5 eV.[13,14] The lower value measured for the reactivation of the $EL2$ reflects the fact that $EL2$-H complex is less stable then the shallow dopant-hydrogen complexes.

The role of the reverse bias on the reactivation of the $EL2$ was investigated. Figure 5 shows the $EL2$ peak height as a function of annealing time for Si-doped GaAs samples annealed at 384 K under zero bias and under reverse biases of 4 V and 8 V. It may be seen the zero bias reactivation of the $EL2$ is much slower than that for the two reverse bias anneals. The slight difference in the -4 V and -8 V anneals is within the sample to sample variation. These results suggest that it is not the magnitude of the electric field that is important. In the case of the reactivation of shallow dopants it has been established that the application of an electric field during annealing results in lower dissociation energies than those reported for zero bias annealed samples.[15] It is believed that significant retrapping occurs if the charged hydrogen species is not drifted away from the dopant. A similar explanation may be invoked for the reactivation of the $EL2$. The amount of hydrogen involved is too small, however, to be detected by passivation of either deep or shallow levels deeper in the material. An alternative explanation for the observed results is that the mechanism of the rapid reactivation is such that it does not occur in the presence of free carriers. It is possible that the greater passivation stability reported by other workers may be ascribed to the fact that no bias was applied during annealing. It should also be noted that differences in passivation conditions can lead to large differences in the amount of hydrogen introduced into the material which further explains the discrepancy between the thermal stability that we have measured and that previously reported.[3,4]

Measurement of the reactivation kinetic parameters under zero bias is complicated by the rapid reverse bias reactivation which occurs when the DLTS peak height is measured. We have ascertained however, that the zero bias reactivation rate at 400 K is at least two orders of magnitude slower than the rapid reverse bias process.

In summary, we have shown that the $EL2$ defect is significantly reactivated by reverse bias annealing at temperatures as low as 366 K. The reactivation may be described by two simultaneous first-order processes, one considerably faster than the other. The kinetics of the rapid reactivation process have been determined and the activation energy has been found to be less than that for the shallow dopants. Thus, while early reports may have indicated that there is a "temperature window"[16] in which the reactivation of shallow dopants could be effected while the electrical activity of deep levels remained supressed, this is clearly not the case for the $EL2$ defect.

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