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A. Vaseashta and L. C. Burton

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Persistent photoconductivity in low-energy argon ion-bombarded semi-insulating GaAs

A. Vaseashta and L. C. Burton
Bradley Department of Electrical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0111

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Time-dependent phototransport measurements are presented for low-energy argon ion-bombarded semi-insulating liquid-encapsulated Czochralski GaAs. Distinct changes caused by ion beam etching were persistent photoconductivity and an increase in photoconductivity. The time dependence of photoconductivity indicated direct participation of the EL2 center. An ion beam induced and optically generated metastable defect state is suggested in the near-surface disordered region to describe the observed phenomena.

From a commercial standpoint semi-insulating gallium arsenide (SI-GaAs) is currently the most used III-V electronic material in the semiconductor industry. Excellent device isolation with reduced parasitic capacitance has provided major improvements for ultrafast computers, microwave radars and communication systems, and electro-optical data transmission systems. One of the key processing steps in the fabrication of GaAs devices is low-energy ion beam etching (IBE), due to its high degree of control, and etch anisotropy. The ion energy utilized in IBE typically ranges from several hundreds of eV to a few KeV. Ion bombardment produces damage in the near-surface regions, which can be categorized as physical, chemical, and electrical. The damage primarily consists of damage to the host lattice, change in stoichiometric composition, introduction of traps in the band gap, and an amorphous layer at the near surface region. The ion beam induced damage and partial amorphization have been extensively reported in the literature for GaAs,1-4 and other substrate materials.5-6 Numerous studies have also been performed to explain an observation of slow-relaxation phenomena termed as persistent photoconductivity (PPC) in Al$_x$Ga$_{1-x}$As alloys,7-12 and in SI-GaAs.13-18 Several models have been proposed to identify the origin of these slow-relaxation phenomena. None of these reports, however, describe a steady-state PPC for ion beam etched GaAs following optical excitation. In this letter, we report our observation of PPC in IBE SI-GaAs and propose a phenomenological model to explain the effect.

The samples used for the present investigation were 8 x 8 mm platelets cut from liquid encapsulated Czochralski (LEC) SI-GaAs wafers having (100) orientation. Samples were thoroughly degreased and chemically etched in a H$_2$SO$_4$:H$_2$O$_2$:H$_2$O (1:2:1 by vol.) solution. Four Au-Ge (88:12)/Ni stripe contacts were evaporated onto each sample followed by a 2 min 440 °C anneal in forming gas to provide ohmic contacts. Samples were treated with HCl:H$_2$O 1:1 (by vol.) at room temperature for 10 min to remove surface oxide, and were then Ar$^+$ ion bombarded in a Perkin-Elmer 5300 XPS system equipped with a model 04-300 differentially pumped ion gun, mounted at 45° with respect to a line perpendicular to the sample surface. The samples were further oriented such that ion bombardment was in the (111) direction. Ar$^+$ ion bombardment was carried out at 1 and 3 KeV energies using a 1 cm$^2$ rastered beam with ion current in the range of 0.2-40.0 µA. The time of ion bombardment was adjusted to provide a fluence of 10$^{16}$ ions/cm$^2$. The samples were attached onto electrically insulated TO-8 headers and 3 mil gold whisker leads were then bonded for the measurements. A given sample was mounted on the cold finger of a variable temperature, optical cryostat having high thermal inertia. Monochromatic excitation was provided by a Gemini Arc lamp, a Jarrell Ash monochromator, and by employing an appropriate set of optical filters. The system was interfaced to an IBM-PC/AT and controlled using Asyst software. A complete description of the optical characterization system has been described elsewhere.17

The photoconductive response depends strongly on the duration of excitation, wavelength, and substrate temperature. The response further depends upon the ion beam energy (virgin, 1 and 3 KeV). dc spectral response curves are shown in Fig. 1. The unquenched spectra showed a rather narrow minima at about 0.80 eV, a broad central peak from 0.9 to 1.5 eV, and a fairly flat region beyond 1.6 eV. The shape of the broad central peak depended on illumination time at each wavelength (illumination time for Fig. 1 was 60 s), indicating an optical quenching behavior, which is later attributed to metastable defect state formation. The response towards the low-energy optical excitation region (< 0.80 eV) was not altered much by the ion etch. These results were in accordance with the results reported by Nojima.13

Photocurrent-time characteristics at 77 K for these photon energies are shown in Fig. (2), and exhibit several interesting features.

(a) The rather slow rise in photocurrent after an initial increase at below band-gap energy excitation (0.80 eV, 1550 nm; 1.19 eV, 1040 nm), and the rapid increase for above band-gap energy excitation (2.06 eV, 600 nm) were strikingly similar to the results reported by Desnica and Santic.18 The sharp rise for the 2.06 eV curves was attributed to the rapid equilibrium of electron-hole pair genera-

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$^a$Also at: Kobe Steel Research Laboratory, 79 T. W. Alexander Dr., Research Triangle Park, NC 27709.

$^b$Now at: Department of Electrical and Computer Engineering, The Pennsylvania State University, University Park, PA 16802.
FIG. 1. Spectral response (current per incident photon) for virgin, 1 KeV etched and 3 KeV etched samples at 77 K (60 s soak time at each wavelength).

The slow rise of the below band-gap curves can be attributed to the slower generation of free carriers due to EL2 photoionization. The unetched sample, however, showed a slight decrease in photoconductivity at 0.8 eV, indicating competition between mid-gap level transitions as proposed by Lin and Bube,19 and probably reduced absorption by the EL2 center.20

(b) The degree of photosensitivity increased by the ion etch. The light to dark conductivity ratio for IBE samples increased by approximately 3000 at 1.2 eV, as compared to 103 at 2.1 eV, clearly indicating the interplay of traps. This increased photosensitivity was due to the increase in dark resistivity. In the presence of optical excitation, traps become filled, increasing the drift mobility, and hence the photoconductivity approached a value comparable to the virgin sample.

(c) There is a considerable PPC evident in the ion-etched samples, with none evident for the virgin samples. Persistent photoconductivity was clearly a distinct signature of the IBE, with a memory effect existing for an extended period of time. The relaxation rates differ considerably for these samples, indicating interplay of the distributed traps within the band gap. We have reported elsewhere how the DLTS response of IBE samples indicated the formation of several distinct traps within the band gap.21 In addition to our current observation for the ion-bombarded samples, PPC has also been observed in SI-GaAs, and in Al1-xGaAs, however no single model proposed so far satisfactorily explains the slow-relaxation phenomena in these materials.

It is well known that ion bombardment produces a highly disordered region near the surface of the target material. Chemical analyses of the disordered region indicated As deficiency as a result of preferential sputtering of arsenic, and an increased surface chemical reactivity.22 IBE introduces discrete trap centers over a region deeper than the ion range predicted by the LSS range distribution theory.23 A possible mechanism for the PPC is the existence of longer lifetime electron traps in the damaged and partly amorphous near-surface region. At lower temperatures (< 120 K) the photoexcited electrons face an energy barrier for recapture. Upon terminating the excitation source due to insufficient energy for recapture, the traps remain ionized resulting in higher conductivity existing over an extended period of time. These could be the same electron traps which result in the low-frequency capacitance dispersion reported elsewhere8 for ion beam etched Schottky diodes (analogous to the persistent photoconductance reported here, no significant dispersion was seen for diodes fabricated on unetched substrates).

A second mechanism for the PPC could be the photogeneration of metastable states which had smaller capture cross sections for electrons. Such states may be associated with metastable complexes formed between EL2 centers and in the ion beam induced defects. In the absence of optical excitation, electronic transitions between the metastable defect configuration and the bands were forbidden, resulting in a larger relaxation time. Thermal activation at T > 125 K provided enough energy for transformation back to the original, stable EL2 state. We can represent such a transformation involving EL2 and an ion beam induced defect X as follows:

optical transformation at 77 K (0.90 eV < hv < 1.4 eV)

\[(X,EL2) \rightarrow (X,EL2)\]

thermal transformation at T > 125 K

\[(EL2,X)^* \rightarrow (EL2,X)\]

where the complex (EL2,X)* was a metastable defect state. This assumption was supported by the physical model proposed by Levinson24 which dealt with the charge state controlled electrostatic interaction between two or more defects. A phenomenological model of the optically generated metastable defect state formation by ion beam...
FIG. 3. Phenomenological model of the optically generated metastable defect state formation by ion beam etching, at (a) room temperature, and (b) $T < 120$ K.

etching was thus proposed, and a flat-band energy diagram is shown in Fig. 3 to elucidate the model. The schematic suggests the formation of $(\text{EL}_2, X)$ defect states within the band gap with no transition pathways to and from the conduction and valence bands.

In summary, $\text{Ar}^+$ ion etching in the 1-3 KeV energy range caused significant changes in the photoconductive response of semi-insulating GaAs. Some of the salient features were: (a) substantial reduction in dark conductivity, (b) increased photosensitivity, and (c) persistent photoconductivity that was not evident in the virgin samples. A possible mechanism for the PPC is the optical generation of metastable states involving EL2 centers and ion beam induced defects. When this complex is in its metastable state during and following optical excitation, the capture cross section for free carriers is reduced, resulting in the persistent photoconductivity.

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