Impact ionization of free excitons in stressed pure germanium

A. Uddin, H. Nakata, and E. Otsuka
Department of Physics, College of General Education, Osaka University, Toyonaka, Osaka 560, Japan
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The low-temperature photoluminescence of free excitons in pure Ge is studied in a weak electric field under uniaxial stress. The photoluminescence intensity of free excitons suddenly drops due to the impact ionization of excitons with increasing applied electric field. On the other hand, the photocurrent sharply increases for the same reason. The breakdown electric field for the impact ionization of excitons decreases to around 40% at 44 MPa in ⟨111⟩-stressed Ge from the zero-stress value. We speculate that this decrease is due to the decrease in binding energy of the exciton with stress.

The effect of uniaxial stress on free excitons (FE) has been investigated in pure Si and Ge. We have found interesting behavior for FE with stress.[1-3] The free-exciton photoluminescence (PL) intensity sharply decreases with stress in pure Si and Ge. The reason for this decrease is not very clear, so we try to draw new information by applying an external electric field to pure Ge at 4.2 K. We have observed impact ionization of free excitons in Ge with uniaxial stress. The breakdown electric field for the impact ionization of FE(LA) decreases to around 40% at 44 MPa from the zero-stress value. We are speculating that this decrease of breakdown field for the impact ionization of FE(LA) is due to the decrease in excitonic binding energy with uniaxial stress. A similar effect has also been observed by other authors in far-infrared magnetoabsorption measurements of excitons in ⟨111⟩-stressed Ge.[4,5] The estimated binding energy of FE in Ge is 2.7 meV at high stress. At zero stress it is 4.2 meV.[6] To our knowledge, no report is available about the impact-ionization measurements of FE in Ge under uniaxial stress.

Free-exciton PL intensity suddenly drops at around 39 V/cm at zero stress in our sample. This breakdown field is much higher than the theoretically predicted value.[7] Experimentally, other authors have also observed the breakdown field of 3–10 V/cm in Ge.[8,9] They predict this breakdown field to depend not only on the binding energy of FE, but also on the impurity concentration as well as on the intensity of excitation power. The critical breakdown field increases in proportion to the square root of excitation power and linearly with shallow impurity concentration in Ge.[9,10] Sclar and Burstein have found that the breakdown field for impact ionization is inversely proportional to the carrier mobility.[11] The mobility of carriers is controlled by the concentration of impurities. These authors further observe that the breakdown field for impact ionization of indium in Ge at 4.2 K varies from 6 to 30 V/cm depending on the concentration of indium. They also observe no breakdown field up to 100 V/cm in undoped Ge and some Ge samples doped with shallow impurities. Similar types of anomalous properties have also been observed by other authors.[12] No explanation is given so far, however.

More recently, Weman *et al.*[13,14] observed a breakdown field of 100–200 V/cm for the impact ionization of FE in Si at low temperatures. They applied an electric field along the ⟨110⟩ direction. The theoretically predicted break down field for the impact ionization of FE in Si is around 20 V/cm at 15 K, irrespective of direction.[7] Such a big difference between the experimental and theoretical values may partly be due to the contact resistance. We find that our sample resistance does not change with stress (up to 80 MPa) in the dark. But under illumination, it sharply decreases with increasing stress. This is due to the increase of free carriers with stress which is consistent with the decrease of PL intensity of FE. The electric-field-determined effective mass of ⟨111⟩ electrons in Ge is nearly 15 times as large as that of other valley electrons for the application of an external electric field along the ⟨111⟩ direction. In Si, the corresponding mass ratio becomes nearly five for the field along the ⟨100⟩ direction. In Ge, the ⟨111⟩ valley becomes the so-called "down-valley" on the stress application along ⟨111⟩. Electrons in the ⟨111⟩ valley, accordingly, will play the most important role in the transport. The reason why a high electric field is required for the impact ionization of excitons in our sample may thus be due mainly to the field-determined directional effective mass of carriers.

The photocurrent sharply increases when the applied electric field exceeds the breakdown (or critical) field. It becomes saturated when the FE concentration becomes zero. With stress application, this saturation behavior of photocurrent changes very sharply. The ionization energy of neutral impurities, as well as excitons, may change with stress. The saturation behavior of photocurrent, accordingly, can change by impact ionization of residual impurities as well as excitons. The application of stress and external electric field changes the balance between ionization and the formation process of excitons. It modifies the relative concentration of excitons and free carriers. An exciton in a semiconductor can be ionized by a number of processes: thermal dissociation (by phonon absorption), collision with a free carrier, etc.

The sample used for the experiment was pure Ge. It was carefully polished by diamond paste and slightly

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etched in CP4A solution ($HF:CH_3COOH:HNO_3$, 5:3:3) to reduce the surface recombination of carriers. The sample dimensions were $1\times1\times2.6$ mm^3. The impurity concentration was $\sim10^{12}$ cm^{-3}. The sample resistance was 50 kΩ at room temperature, 2.3 MΩ at 4.2 K in the dark, and 0.2 MΩ with illumination. Ambient light such as blackbody radiation may have an effect on the sample resistance at 4.2 K in the dark. The sample resistance became around 1 kΩ when the applied electric field exceeded the critical field at zero stress. With stress this high-field resistance became less than 1 kΩ. The sample was excited by an Ar^+ laser of 300 mW at $\lambda=514.5$ nm and the incident power was kept constant throughout the experiment. The Ar^+-laser beam was mechanically chopped at 200 Hz. Thin electrical wires were connected by soldering with the upper copper stress head. The lower connection was made by silver paint with the aluminum foil on which the sample sat in contact with the lower stress head. The sample resistance remained the same in changing the polarity. Even at "zero stress" the sample always underwent a little stress (~1 MPa) due to the weight of the stress rod and a spring. The PL signal was analyzed by a high-resolution monochromator and was detected by a Ge *p-i-n* photodiode, cooled to 77 K. The detected signal was recorded through a conventional lock-in amplifier. The electric field was applied by a dc power supply. The photocurrent and applied voltage were measured by the digital meters. The current-induced sample heating was at most ~1 K at an electric field higher than the breakdown field. The uniaxial stress and electric field were applied along the ⟨111⟩ direction. Stress homogeneity was checked by PL measurements of the FE luminescence. No broadening of the exciton peak was observed with stress. Stress homogeneity was also checked by time-resolved measurements of the FE luminescence. No change of the exciton peak position was observed for different delay times. These indicated highly homogeneous stress conditions on our sample.

Figure 1 shows the PL spectrum from pure Ge at zero stress. The FE(LA) line is stronger than other phonon-assisted emissions in Ge. We have mainly investigated the behavior of FE(LA) emission with stress and electric field. The luminescence intensity of FE(LA) is stronger than that of electron-hole-liquid EHL(LA) line. The EHL(LA) peak disappears at around 16 MPa. We have observed no bound-exciton lines from our pure Ge samples.

The luminescence intensity of FE(LA) drastically decreases with increasing stress as shown in Fig. 2. At zero electric field the FE(LA) luminescence intensity decreases to around one-tenth, at 44 MPa, in comparison with the zero-stress luminescence. The decrease in luminescence is nearly linear with stress for low stress. At zero stress the FE(LA) luminescence intensity remains almost constant against applied electric field up to 23 V/cm. Then it decreases a little. At an electric field of ~39 V/cm, the FE(LA) luminescence intensity suddenly drops. So we can say that 39 V/cm is the critical field for impact ionization of FE in Ge at zero stress. For the field range of 23–38 V/cm, we can see unstable behavior of the FE PL intensity at zero stress. That may be reflecting an effect

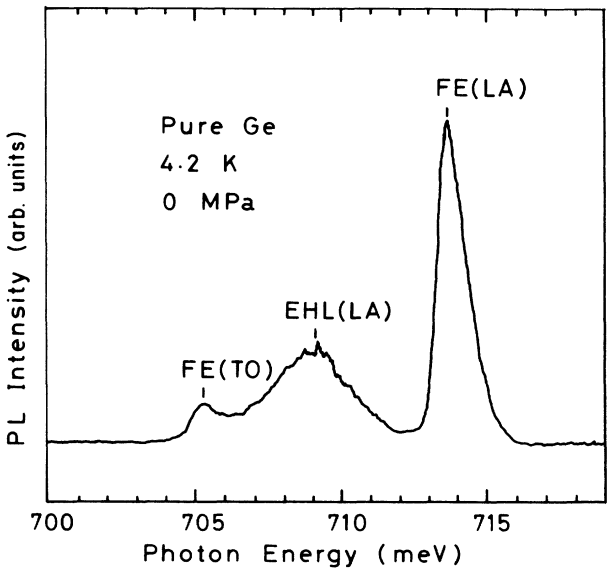

FIG. 1. Photoluminescence spectrum at 4.2 K of phonon-assisted recombination of free excitons and the electron-hole pair in an EHL in pure Ge at zero stress. The peak energies of FE(LA), EHL(LA), and FE(TO) are 0.714, 0.709, and 0.705 eV, respectively.

from the EHL(LA), since the EHL luminescence intensity starts to decrease after 23 V/cm. With increasing stress, the critical field for impact ionization of the exciton decreases. This decrease in critical field is nearly linear with stress. The breakdown field of free excitons, however, seems to give a steady value at high stress. The

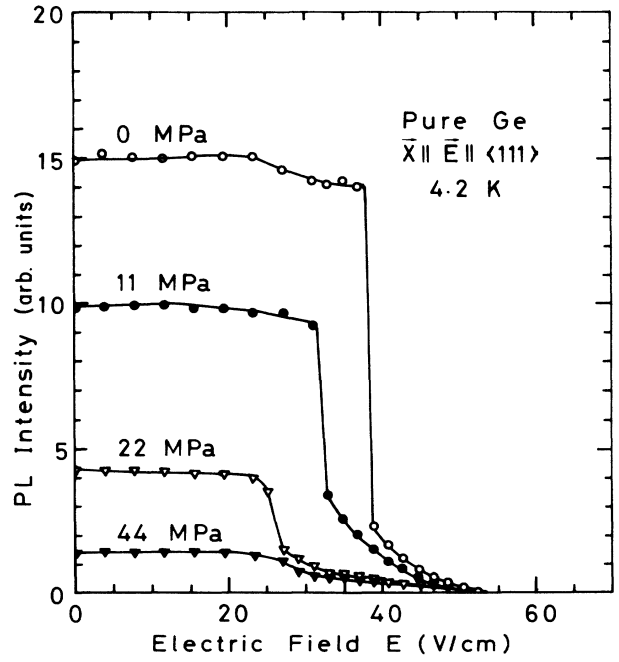

FIG. 2. The PL intensity of the FE(LA) peak under different stresses as a function of electric field at 4.2 K. At zero field the PL intensity of FE(LA) decreases to about one-tenth at 44 MPa compared wit the zero-stress luminescence. The stress and electric field are applied along the ⟨111⟩ direction.

critical field for the impact ionization of excitons decreases from 39 V/cm at zero stress to 24 V/cm at 44 MPa. The decrease in critical field strength is around 38% at 44 MPa compared with the zero-stress critical field strength.

For zero stress, it is reported, at 5 K, that the breakdown field is linearly related with the ionization energy of shallow or deep impurities.[15] Excitons in a semiconductor have properties very similar to hydrogenic impurities. Under stress, it is not clear how the breakdown field will be related with the excitonic binding energy or impurity ionization energy. If we presume a linear relation, the binding energy of FE in Ge will be 2.6 meV at 44 MPa, which agrees with other authors' values.[4,5]

The spatial distribution of excitons in our sample was $n_{ex}/n_{0ex}=2\exp[-a/(D_{ex}\tau_{ex})^{1/2}]=0.67$, where n_{0ex} is the exciton concentration on the excited surface, n_{ex} the exciton concentration on the opposite surface, $a=0.1$ cm the sample thickness, $D_{ex}=1500$ cm^2/s the diffusion coefficient of the exciton,[16] and $\tau_{ex}=5.6$ μs the exciton lifetime.[2] Two surfaces of the sample were excited simultaneously. While forming excitons, free carriers can diffuse a certain distance through the sample, even as far as the opposite surface of the sample, owing to the high diffusion coefficient. Actually $n_{ex}/n_{0ex}>0.67$. The spatial distribution of long-lived indirect excitons in such a small sample piece thus turns out to be pretty homogeneous.

The rate of change in exciton concentration is controlled by the rates of exciton recombination, thermal dissociation (by phonon absorption), impact ionization, and formation. The rate equation for the exciton concentration n_{ex} is written as

$$dn_{ex}/dt=G_{ex}-n_{ex}/\tau_{ex}-\alpha_{ex}n_{ex} - A_e n_{ex} n_e - A_h n_{ex} n_h \ , \quad (1)$$

where $G_{ex}=\nu_{ex}n_e n_h$ is the generation rate of excitons with $\nu_{ex}=5.1\times10^{-5}$ cm^{3}s^{-1} (4.2 K) being the binding coefficient of excitons, α_{ex} the thermal dissociation coefficient of excitons, and A_e and A_h the coefficients for electron-impact and hole-impact ionization of excitons, respectively, while n_e and n_h are the free-electron and hole concentrations, respectively. At low temperatures, very few free carriers have enough energy for the impact ionization of excitons. Hence the second line of Eq. (1) is negligible at zero electric field. In the steady-state condition, Eq. (1) should be equal to zero. The thermal dissociation coefficient is expressed as

$$\alpha_{ex}=\nu_{ex}(2\pi\mu k_B T/h^2)^{3/2}\exp(-E_x/k_B T) \ , \quad (2)$$

where E_x is the binding energy of the exciton and μ is the reduced mass of the exciton, defined as $1/\mu=1/m_e+1/m_h$, where $m_e=0.22m_0$ and $m_h=0.3m_0$ are the effective masses of the electron and hole, respectively, m_0 being the electronic rest mass. The quantity $G_{ex}=5.1\times10^{19}$ cm^{-3}s^{-1} is calculated by using the relation $G_{ex}/P=1.7\times10^{20}$ cm^{-3}s^{-1}W^{-1},[9] neglecting the nonradiative recombination of free carriers. Under different stresses we have calculated α_{ex} and n_{ex} by using Eqs. (1) and (2) as shown in Table I, assuming that τ_{ex} and ν_{ex} are independent of stress and μ is linearly decreasing with E_x. When a stress is applied, α_{ex} tends to increase on account of the decrease in binding energy of FE. At zero electric field the PL intensity $I_{FE}=Bn_{ex}$, where B is a constant. If B were independent of stress, n_{ex} at 44 MPa should be lower by an order of magnitude than its zero-stress value, since at 44 MPa PL intensity becomes one-tenth its zero-stress value. The calculated value of n_{ex}, however, is lower by almost 2 orders of magnitude. It thus seems that B cannot be independent of stress. One should further note that G_{ex} will also decrease due to the decrease in binding energy of FE. We may thus speculate that the decrease in PL intensity of FE(LA) at zero electric field is due mainly to the decrease in binding energy of FE with uniaxial stress.

A free carrier is accelerated under the influence of the electric field until it makes a collision. At low temperature, the rate of energy loss by collisions can be expressed as[11]

$$E_s=m^2v^2/\tau M \ , \quad (3)$$

where $1/\tau$ is the rate of collision, m^2v^2/M the average energy loss per collision, m the effective mass of the free carrier, v the speed of the carrier, and M the mass associated with the exciton or lattice vibrations and equal to $k_B T/c^2$ depending on the collision, where c is the longitudinal velocity of sound.[11] The kinetic energy of a free carrier is built up over a number of mean free paths until it becomes sufficient to ionize an exciton or a neutral impurity by impact. Whereas the exciton ionization by phonon absorption is not significantly affected by an electric field. The impact-ionization cross section, however, contains a threshold owing to the excitonic binding energy. Accordingly, as the field accelerates carriers to energies comparable with the excitonic binding energy, the impact-ionization coefficients A_e and A_h in Eq. (1) will increase sharply, as reflected in the photocurrent measurement shown in Fig. 3. Sclar and Burstein[11] indeed give an expression for the critical field E_c for the onset of

TABLE I. Breakdown field E_c, FE binding energy E_x, thermal dissociation coefficient α_{ex}, and FE density n_{ex} under different uniaxial stresses at zero electric field at 4.2 K in pure germanium.

Stress X (MPa)	E_c (V/cm)	Corresponding E_x (meV)	α_{ex} (s^{-1})	n_{ex} (cm^{-3})
0	39.0	4.20	2.1×10^5	1.3×10^{14}
11	33.0	3.55	1.0×10^6	4.3×10^{13}
22	28.0	3.02	3.8×10^6	1.3×10^{13}
44	24.0	2.58	9.2×10^6	5.4×10^{12}

breakdown:

$$E_c=(m/q\tau M^{1/2})[2\beta E_x(1-2k_BT/\beta E_x)]^{1/2} . \quad (4)$$

Here q is the free-carrier charge and β a fractional quantity less than unity, or βE_x the kinetic energy of a free carrier at which breakdown is expected. For impact ionization of FE at 4.2 K we have found $\beta\sim 0.2$ for both electrons and holes at zero stress, assuming $1/\tau=1\times 10^9$ s^{-1} for electrons and 2×10^9 s^{-1} for holes.[17]

At zero stress, the photocurrent increases very sharply when the field exceeds the critical field for the impact ionization of excitons. The photocurrent is saturated around 60 V/cm, corresponding to the vanishing of excitons as shown in Fig. 3. Presence of this saturation indicates that free carriers are not sufficiently energetic yet for impact ionization of residual impurities. With uniaxial stress, the saturation of photocurrent tends to disappear. This may indicate that the ionization energy of impurities decreases with stress.

The uniaxial stress along the ⟨111⟩ direction in Ge removes the degeneracy and significantly simplifies the conduction and valence bands at $k=0$. This causes a decrease in hole effective mass. The decrease in effective mass results in a decrease in binding energy of the exciton. The effective mass of the free carriers dominant in transport under a strong electric field, especially that of electron, changes with the electric field.[18] The energy loss of a carrier by collision is also affected in accordance with Eq. (3). Under stress, furthermore, most of the holes and electrons are concentrated in the bands of lowest energy. The excitonic states are built out of one electron valley and one hole band; both are ellipsoids with principal axes along ⟨111⟩. In that case the excitonic structure becomes more hydrogenic. When an electric field is applied, the electron and hole will undergo transitions into the higher-lying valley or band. The heated carriers can easily ionize the neutral impurities by collisions.

In conclusion, the PL intensity of FE(LA) decreases to around one-tenth at 44 MPa compared with the zero-stress luminescence at zero electric field. The PL intensity of FE(LA) suddenly drops due to the impact ionization of excitons by free carriers with increasing electric field, whereas the photocurrent sharply increases on account of the same reason. The breakdown field of an exciton in Ge decreases to around 40% at 44 MPa compared to the zero-stress value. The decrease in zero-field PL intensity and in breakdown field indicates a decrease in binding energy of FE with uniaxial stress. The ionization energy of impurities also seems to decrease with stress.

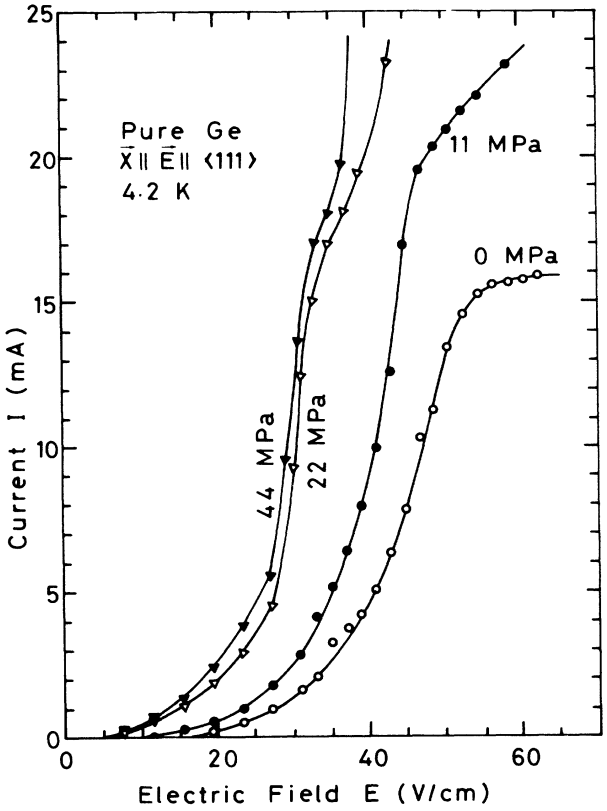

FIG. 3. The photocurrent at 4.2 K as a function of applied electric field at different stresses. When the applied field exceeds the critical field, corresponding to the binding energy of the exciton, the photocurrent sharply increases due to the impact ionization of excitons. For zero stress, however, the current shows a saturation at high field.

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