Defect creation by subthreshold irradiation in semiconductors

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Defects are created in a crystal lattice by irradiation when the incident particles displace atoms from their substitutional positions. When the mechanism is elastic scattering, displacement occurs when the energy transmitted by the incident particle, T, is greater than T_d, the threshold energy. It has been argued, however, that defects can also be created in semiconductors for $T < T_d$ through mechanisms involving electron excitation. The occurrence of such mechanisms has not been demonstrated conclusively because effects related to surface states or impurity diffusion cannot be discounted in the experiments which have been reported. To obtain further evidence of intrinsic subthreshold defect production, we have used a transient-capacitance technique which is appropriate because it can detect low defect densities, measure the distribution of defects below the surface of the crystal, and distinguish individual defect species. Because we do not see any defects, which implies defect introduction rates lower than 2×10^{-8} cm^{-1}, in both silicon and germanium irradiated with electrons of below-threshold energy, we conclude that intrinsic point defects are not created by subthreshold irradiation.

INTRODUCTION

Defects are created in a crystal lattice by irradiation when the incident energetic particles displace atoms from their substitutional positions, creating vacancy-interstitial pairs. Atomic displacements occur when the energy transmitted to the lattice atoms is larger than a certain value, T_d, the threshold energy. This concept of threshold energy is well established in the case of electron irradiation by the fact that the variation of the defect production with the energy of irradiation can be fit very well by the Rutherford scattering cross section using a single value of the threshold energy as a parameter. An example of this is given in Ref. 1 for defects in GaAs introduced by electron irradiation. Actually the threshold energy varies slightly with the direction of the incident electron beam relative to the crystallographic orientation because, as was clearly demonstrated by Pons,[2] the displacement cross section depends also on the interaction of the primary knock-on atom with its neighbors.

Defect creation by electron irradiation has been studied extensively in semiconductors but often the value of the threshold energy has not been determined accurately. It is found to be approximately 15 eV (11—22 eV) in silicon, which corresponds to an electron energy of 130—250 keV, and about 20 eV (13—30 eV) in germanium, which corresponds to an electron energy of 350—620 keV.[3] Details of the calculations of collision cross sections and displacement energies can be found in Ref. 4, for example. In addition to the defects introduced by the direct collision mechanism, subthreshold defects, i.e., defects introduced by incident particles whose energy is such that they cannot transmit an energy equal to or larger than the threshold energy to the lattice, have been said to be produced in various semiconductors.[5—7] Because such subthreshold defects cannot be attributed to atomic displacements caused by direct collisions, the transmitted energy being smaller than T_c, they can only be related to the electronic excitation which accompanies the irradiation. Several mechanisms have been proposed to explain defect production by subthreshold irradiation.[5] For instance, the ionization of an atom is said to induce its displacement in a fashion similar to that which occurs in ionic materials[8—11] where, schematically speaking, the multiple ionization of an atom results in its expulsion from a substitutional site due to the Coulomb repulsion by the neighboring ions.

Electronic excitation can induce atomic processes in semiconductors. This is clearly documented in the case of ionization-induced migration of defects and impurities.[12] However, that electronic excitation can result in defect production has not been clearly demonstrated. As discussed in Ref. 12, the experimental evidence for the production of these defects is not unambiguous. Defects said to have been introduced by subthreshold irradiation can be classified into two categories: (1) extrinsic effects in which it is clearly demonstrated that the production of subthreshold defects is caused by the presence of light impurities, e.g., H in Ge (Ref. 13), and (2) effects which can be interpreted as changes of surface states in thin films resulting in a change in their luminescence or resistivity, as impurity diffusion at electrical contacts, etc.

In order to obtain unambiguous evidence of the existence of intrinsic subthreshold defect production, it is necessary to use a technique which fulfills the following criteria: (1) It must be sensitive because the defect introduction rate is expected to be small, (2) it must be spectroscopic in order to allow the identification of the created defects or at least to observe them individually, (3) the technique should be able to determine the spatial distribution of the defects in order to distinguish between created defects and diffusing impurities or defects, and (4) it should be able to detect defects below the surface of the crystal so that spurious effects such as those due to changes of surface states may be eliminated. Deep-level transient spectroscopy[14] (DLTS) which analyzes the emission of charges from localized states in the space-charge region of a junction or Schottky-barrier diode meets all these requirements. This technique has been used to study defects introduced by electron irradiation (electron energies of the order of 1 MeV) in both silicon and germanium, and defects associated with the vacancy have been identified in both materials.[15–18] For these reasons we have used DLTS to study the production of subthreshold defects in silicon and germanium. If atomic displacements are produced by irradiation at room temperature with electrons of energy less than the threshold energy, vacancies will be produced and, because the vacancy is mobile, complexes involving the vacancy should be observed. In this paper we report results for both silicon and germanium since the subthreshold effects have been studied and the defects are best known in these materials.

EXPERIMENTAL DETAILS

The silicon diodes used for this experiment were Schottky-barrier diodes fabricated by electron-beam evaporation of 200 Å of Pd followed by 2000-Å Au through a metal mask on (5–10)-Ω cm Czochralski-grown silicon wafers. Schottky diodes were also fabricated on unirradiated wafers which were measured to be sure that any process-induced defects were not mistaken for radiation-induced defects.

Irradiations were done at room temperature using a 3-MeV Van de Graff accelerator with electron energies above threshold (1 MeV) and just below the assumed threshold (50–100 keV). The electron beam was scanned over an area large compared to the sample area in order to ensure a uniform fluence. The low-energy irradiations were performed in two ways. One group of samples was irradiated with the electron energy set at 100 keV which ensured incident electrons of energy between 50 and 150 keV. The uncertainty of the electron energy is due to the poor stability of the machine for such low-energy electrons. The fluence was 3×10^{17} cm^{-2}. Because the flux obtained in this way is rather small, we also used a second method in which higher-energy electrons were used and the sample was placed behind another silicon wafer in order to decrease the electron energy to the desired average value. The sample was placed behind a silicon wafer 0.666 mm thick and a 650-keV electron beam was used. The energy of the electrons reaching the sample is 100 keV with an uncertainty of 50 keV. The fluence for these samples was 1×10^{17} cm^2. Another group of samples was irradiated with electrons well below threshold energy (10 keV) using a simple electron gun. The beam was not scanned so the fluence was not uniform over the wafer surface. The average fluences in this case were 1×10^{17}, 1×10^{18}, and 1×10^{19} cm^{-2}.

The germanium diodes used for this experiment were identical to those used for studies of defects introduced by 1-MeV electrons.[17,18] They are commercial p^+-n photodiodes with a carrier concentration at room temperature of 3×10^{13} cm^{-3}. The substrate dopant is unknown. The subthreshold irradiation was done with 250-keV electrons to a fluence of 5×10^{16} cm^{-2} using the 3-MeV accelerator. Each diode was measured both before and after irradiation.

The DLTS system we used is similar to that described in Ref. 1. The capacitance transient is analyzed using a two-phase lock-in amplifier giving a sensitivity of about 10^{-4} times the free-carrier concentration in the material. Diodes were measured in the temperature range from 77 to 350 K. The reverse-bias voltage was 2.0 V and the amplitude of the filling pulse varied from 1.0 to 2.0 V so that traps close to the metal/silicon interface, for example, were not measured. This was necessary to reduce the effect on the spectrum of near-surface defects introduced during diode fabrication in the case of silicon.[19]

RESULTS

Figure 1 shows the DLTS spectra of silicon wafers irradiated with 100-keV and 1-MeV electrons. The peaks labeled E_1–E_4 have been observed before in electron-irradiated silicon: E_1 is the V-O pair (A center), E_2 and E_4 are the singly and doubly negatively charged states of the divacancy, and E_3 has not been identified.[16] E_5 is a defect which was introduced during electron-beam deposition of metal to form the Schottky-barrier diodes. A detailed description of the conditions under which it is introduced are published elsewhere.[19] Varying the filling-pulse amplitude as is shown in Fig. 1(b) shows that E_5 occurs only near the metal/silicon interface. E_6 [Fig. 1(a)] has not been identified.

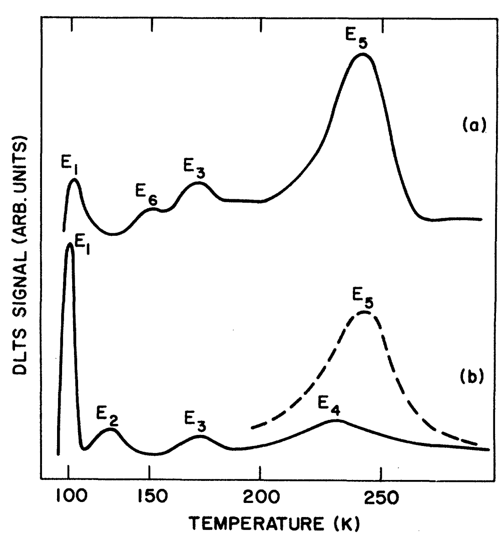

FIG. 1. DLTS spectra of silicon Schottky diodes irradiated with (a) 100-keV and (b) 1-MeV electrons. $V_B=2.0$ V. $V_p=1.0$ (solid curves) or 1.5 V (dashed curve). The rate window was 8.7 msec.

Comparing the two spectra, we see that in both cases the V-O pair is present. In the diodes irradiated with near-threshold energy electrons the divacancy was not observed. This is reasonable since the divacancy could not be created directly by a single electron of this energy (its threshold energy for direct production is $2T_d$) and the introduction rate for the creation of single vacancies is so low that the divacancy seems not to be formed by the combination of single vacancies. The spectrum for diodes irradiated with 10-keV electrons is not shown since only E_5, the defect introduced during diode fabrication, was observed. Neither the divacancy nor the V-O pair were seen in samples irradiated with 10-keV electrons.

The change in the free-carrier concentration determined at room temperature by C-V measurements is a reliable measure of total trap concentration. For the samples whose spectra are shown in Fig. 1, the diodes were fabricated prior to irradiation. Thus the total introduction rate for the electron-irradiation-induced defects can be estimated from the change in the free-carrier concentration. The free-carrier concentration measured for irradiated diodes is about 50% of that measured in unirradiated diodes. For 1-MeV electrons the introduction rate is $\sim 0.4\ \text{cm}^{-1}$ and for 100-keV electrons it is $\sim 2\times 10^{-3}\ \text{cm}^{-1}$. In the case of 10-keV electrons an upper limit for the introduction rate can be calculated. The sensitivity of the measurement is $\sim 10^{-4}$ of the free-carrier concentration which was $5\times 10^{14}\ \text{cm}^{-3}$. The largest fluence used was $10^{19}\ \text{cm}^{-2}$. Thus the introduction rate is lower than $5\times 10^{-9}\ \text{cm}^{-1}$.

DLTS spectra for germanium diodes irradiated with 1- and 2-MeV electrons have been published and both vacancy- and divacancy-related defects have been identified.[17,18] In Fig. 2 we show the spectra for diodes irradiated with 540-keV ($10^{16}\ \text{cm}^{-2}$) and 2-MeV ($10^{15}\ \text{cm}^{-2}$) electrons. Only vacancy-related defects (E_1 and E_2) are observed after irradiation with 540-keV electrons while both vacancy- and divacancy-related defects are observed after irradiation with 2-MeV electrons. The spectrum for diodes irradiated with 250-keV electrons is not shown since no peaks were observed. The sensitivity of the measurement is such that defects with a concentration of 10^9 cm^{-3} would be observed. The fluence was $5\times 10^{16}\ \text{cm}^{-2}$ which implies a defect-creation rate of lower than $2\times 10^{-8}\ \text{cm}^{-1}$ for irradiation with 250-keV electrons.

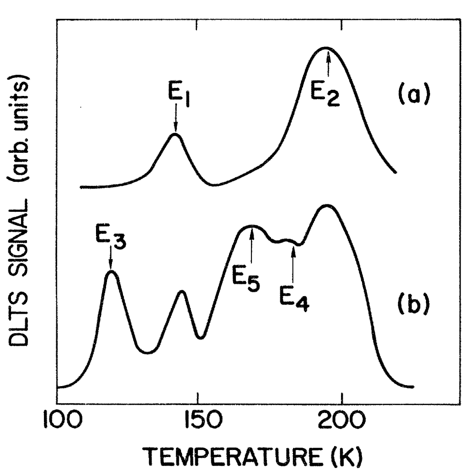

FIG. 2. DLTS spectra for germanium p^{+}-n junction diodes irradiated with (a) 540-keV and (b) 2-MeV electrons. The rate window was 6.9 msec.

DISCUSSION

Defects created by direct displacement or by any other type of process must always be vacancy-interstitial (V-I) pairs. Thus, if the defects are produced by irradiation with subthreshold-energy electrons, what is observed results from the diffusion of vacancies and interstitials and their association with impurities or with themselves (e.g., the divacancy) and should be the same as in the case of direct displacement by electrons with energy greater than the threshold energy. Possible differences observed between the two cases should be in the rate of creation of the defects and also in the relative concentration of the defects since defect mobility and trapping by impurities depends on charge-state effects, i.e., on the electron flux, which are considerably different for above-threshold and subthreshold irradiations. Irradiation with 10-keV electrons in silicon and 250-keV electrons in germanium results in an introduction rate whose upper limit is $2\times 10^{-8}\ \text{cm}^{-1}$. Vacancy-related defects observed in both silicon and germanium irradiated with near-threshold energy electrons are the same as in samples irradiated with 1- or 2-MeV electrons, except for a much reduced introduction rate, suggesting that the published values for the threshold are in error. Because of its high sensitivity, the DLTS technique is a good method to use to determine the threshold energy very accurately (see Refs. 1 and 18).

It is interesting to compare the introduction rates we have measured with those cited in the review articles on mechanisms for subthreshold defect creation (Refs. 4 and 5) to prove the existence of subthreshold defect creation in semiconductors. For example, an introduction rate of $10^{-3}\ \text{cm}^{-1}$ was cited for n-type silicon irradiated with 9-keV electrons and $2.5\ \text{cm}^{-1}$ was cited for n-type germanium irradiated with 300-keV electrons.[6] Looking at the original papers we find that in the first case the authors have shown that their measured value of the displacement cross section is 10 times lower than that predicted by the ionization model and thus claim that displacement after ionization alone is not possible.[20] In the second case subthreshold defects were attributed to the displacement of impurities in the crystal and not to the displacement of germanium atoms.[13,21] Thus both of these experiments are not evidence for the subthreshold creation of defects as claimed in Ref. 6, but in fact are consistent with the results we present here showing that the displacement of atoms does not occur by irradiation with particles of subthreshold energy. Similarly, when conductivity measurements are used to monitor the defect introduction rate in epitaxial layers,[22] the resisitivity changes, which have been attributed to the introduction of defects, are undoubtedly associated with a change of surface states. These states create a space-charge layer and its modification changes the thickness of the layer in which conductivity occurs.

CONCLUSION

Although the measurement technique we have used can detect vacancy-related defects in very low concentrations, the experiments described in this paper show that no deep-level defects were observed in silicon or germanium irradiated with subthreshold-energy electrons. Consistent with our results, the experimental evidence cited previously to support the existence of such defects can be explained by spurious effects such as diffusion of impurities from metal contacts or changes in surface states which result in resistivity changes in thin films. We conclude, therefore, that intrinsic point defects are not created by irradiation with electrons of subthreshold energy.

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