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Effect of laser irradiation on the electrical properties of amorphous germanium films

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Amorphous films of germanium were grown using a vacuum evaporation technique, on glass substrates kept at room temperature. As-grown films were irradiated with Q-Switched Nd-YAG laser pulses (λ = 1.06 μm, 20 nsec, 10 to 50 mJ cm^{-2}). The d.c. conductivity measurements were made in the temperature range 77 to 300 K. It was observed that the effect of laser irradiation was similar to the effect caused by the thermal annealing of the films. The d.c. conductivity data were analysed in the light of Mott's theory of a variable range hopping conduction process.

1. Introduction

Laser irradiation of amorphous or polycrystalline samples causes recrystallization, changes their conductivity and alters their optical properties. During the last few years, laser irradiation has been used for producing solid phase tranisitons, crystallizing amorphous layers, annealing the defect structure and for electrical activation of ion-implanted atoms [1–8]. Both continuous wave, CW [9–10] and pulsed beam mode [1, 11, 12] annealing have been reported using optomechanical scanning of a focused beam. Laser-induced crystallization in amorphous germanium (a-Ge) and amorphous silicon (a-Si) has been widely used by many workers using continuous and low power [9] short pulses with powers of the order of 1 kW per pulse [13–15]. Very short pulses (50 nsec) with power densities in the range 10 to 80 MW per pulse, have been used for crystallizing a-Si [11, 15–17] layers but very little work has been reported on the effect of laser irradiation of these very short pulses on a-Ge. Moreover, it is believed that the very short power pulses cause melting of the amorphous layer which crystallizes on solidification. However, the exact mechanism is still not clearly understood [18]. The physical properties of a-Ge and a-Si depend significantly on the preparation conditions. Films of a-Ge, in particular, prepared by evaporation on to room-temperature substrates contain structural defects which have been established by small-angle scattering [19–22] to consist of regions of missing atoms, i.e. voids. Sometimes the voids in a-Ge are such that the density of the resulting films is about 30% less [23] than that of crystalline germanium. The presence of these voids and other defects during growth gives rise to the states in the pseudogap [24–28] and affects properties such as low temperature d.c. transport, low level optical absorption, and paramagnetic spin density. Lovato and his co-workers [13, 15] have shown that the laser annealing of a-Ge films using repetitive laser pulses of medium power (1 kW/pulse; 10^{-6} sec) crystallizes the a-Ge films and the process is a non-thermal process.

In the present work, a-Ge films grown on glass substrates were irradiated with Nd-YAG, Q-switched laser pulses of 20 nsec duration with power densities in the range 10 to 50 mJ cm^{-2}. The d.c. conductivity studies, in the temperature range 77 to 300 K have been made on the irradiated films. It was observed that the conductivity initially decreases significantly (up to $\sim$ 30 mJ cm^{-2}), with increase of laser power density, and begins to increase with further increase of power density of the laser pulses. The d.c. conductivity data agree well with Mott's theory [29] for a variable range hopping conduction process.

2. Experimental details

Rectangular films of size 20 mm × 4 mm were grown from evaporation grade germanium (Balzers Aktiengesellschaft, Fürstentum, Liechtenstein, Switzerland) by resistive heating under a vacuum of $\sim 10^{-6}$ torr on to glass substrates. The thickness of the films was in the range of 100 to 120 nm and was controlled using a quartz crystal thickness monitor. Films from the same batch were irradiated with a pulsed Q-switched Nd-YAG laser in air (λ = 1.06 μm). The beam diameter was adjusted to be 1.0 cm. The pulse duration was of the order of 20 nsec, and the power density of the laser beam was varied in the range 10 to 50 mJ cm^2. In order to measure the d.c. conductivity, ohmic planar contacts of silver [30] were evaporated on to the films after irradiation with laser pulses. The contacts were spread over the film including a part of the laser-irradiated portion, such that the effective dimensions of the film were 5 mm × 4 mm. The d.c. conductivity measurements were made using a model 610 C Keithley Electrometer. The sample was mounted on a Copper block, with electrical insulation, which was kept in a Dewar flask containing liquid nitrogen.

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A copper–constantan thermocouple, soldered to the copper block, was used to measure the temperature.

3. Results and discussion

Transmission electron microscopy studies indicated that the as-grown films, as well as the films irradiated with laser power densities of $\leqslant 30\,mJ\,cm^{-2}$, were amorphous in nature. However, laser power densities of $> 30\,mJ\,cm^{-2}$ resulted in an improvement in crystallinity.

The films irradiated with a single pulse of power density up to $25\,mJ\,cm^{-2}$ did not show any significant change in their electrical properties. However, when the energy was increased from $25\,mJ\,cm^{-2}$ there was a permanent change in the electrical properties of the films. The observed change increased with the number of pulses and attained the maximum value after 8 to 10 pulses. Further irradiation of the films produced very little changes. There was no significant effect of film thickness on these results in the thickness range studied. The change of properties after a few pulses, i.e. cumulative effect of several pulses, has also been observed by many other workers [31–34]. It has been suggested by Regolini *et al.* [31] that the first few laser pulses cause localized islands. Further irradiation increases the area of these islands and finally converts the whole area into a single region.

Fig. 1 shows the typcial results on the conductivity of the films as a function of power density. The number of pulses used was 10 and the laser was used to give pulses at a rate of 2 pulses per second. It can be observed from this figure that the conductivity decreases initially with increase of laser power density

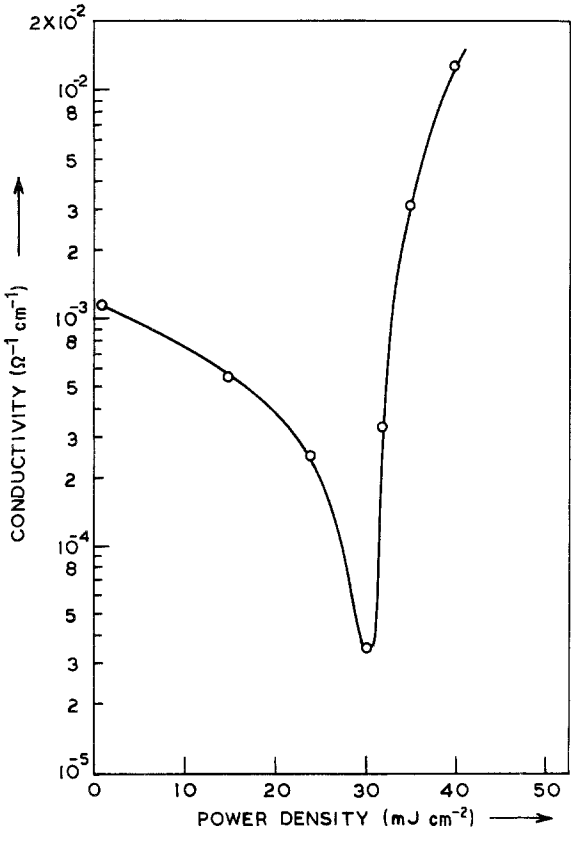

Figure 1 Variation of d.c. conductivity as a function of laser power density (T = 300 K, no. of pulses = 10).

up to $\sim 30\,mJ\,cm^{-2}$, beyond which it increases rapidly. The observed results are slightly different from the earlier reported results on films exposed to laser pulses of shorter durations [13–15]. It has been reported by Lovato *et al.* [15] that the conductivity continues to increase monotonically with increase of laser power density. Chopra and co-workers [35, 36] have, however, reported that when the a-Ge films are subjected to thermal annealing the resistivity increases initially with the increase of annealing temperature, up to a temperature T_c, known as the crystallization temperature, beyond which the resistivity decreases. It is well known [19–22] that amorphous germanium films contain a large number of voids and other defects, which give rise to the extrinsic conductivity observed in the as-grown films. Annealing of these films [24, 35–37] up to the crystallization temperature at which the nucleation growth starts, reduces the number of electrically active imperfections caused by voids and dangling bonds, thus decreasing the conductivity. When the films are annealed beyond T_c, the crystallization begins and the conductivity of the films increases rapidly. Although the value of T_c is quite sensitive to the deposition conditions, the nature of the substrate and the method of detection, its value for thin amorphous germanium films is reported to be ~ 800 K [24, 35, 36]. Croitoru and Marinescu [38] have reported their observations on the barrier height measurements on a-Ge/n-single crystal germanium junctions. They observed that the as-grown films were p-type and the acceptor density was 10^{17} to $10^{19}\,cm^{-3}$. The annealing of these layers reduced the acceptor density significantly and thus increased the resistivity. The present observations suggest that the results of the annealing of a-Ge films with very short laser pulses (~ 20 nsec) with a power density of 10 to $30\,mJ\,cm^{-2}$ are similar to the reported results on thermal annealing of these layers.

When the laser power density was increased beyond $40\,mJ\,cm^{-2}$, there were visible cracks in the films. It may be mentioned that the presence of cracks has not been reported [13–15] earlier for short pulses ($\sim 10^{-6}$ sec) of ultraviolet to visible region wavelengths. A possible explanation for the presence of cracks is as follows: it is known [23, 37–39] that in the annealing of amorphous germanium films, some densification occurs prior to crystallization and results in the appearance of a network of microcracks and small voids [40, 41]. If the temperature of the film is increased very rapidly, then the grain growth occurs very rapidly such that the void/grain boundary interaction [42] is of relatively little importance, and the voids, because of their rapidly decreasing mobilities, merge [43, 44] into the growing crystallites. Since the absorption coefficient of germanium is comparatively smaller at 1.06 μm than at ultraviolet or visible wavelengths, it suggests that the temperature reached in the present case is not sufficient to avoid void/grain boundary interactions.

The variation of d.c. conductivity ($\log\sigma$ against $1000/T$) for as-grown as well as laser-annealed films is shown in Fig. 2. It is found that the conductivity of all the films increases with increasing temperature.

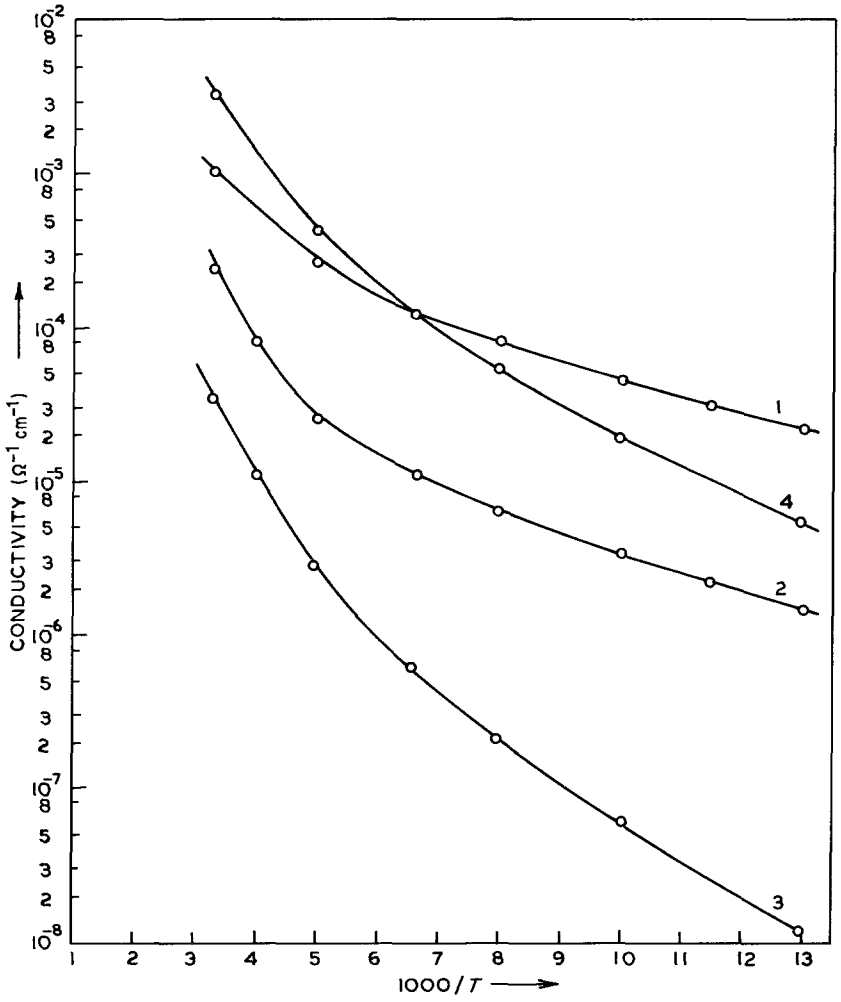

Figure 2 Variation of d.c. conductivity as a function of temperature ($\log\sigma$ against $1000/T$) for (1) as-grown, (2) 24 mJ cm^{-2}, 10 pulses, (3) 30 mJ cm^{-2}, 10 pulses, (4) 35 mJ cm^{-2}, 10 pulses.

However, the rate of increase is slower in the low temperature region (77 to 150 K) and the increase is faster in the high temperature region (150 to 300 K). The observed variation of d.c. conductivity for as-grown films is in good agreement with the results of other workers [41, 45–48].

The low temperature conductivity data have been analysed for the variable range hopping conduction process on the basis of the model proposed by Mott [29, 49] for disordered materials in the following manner.

The conductivity data have been replotted in Fig. 3 as $\log\sigma\, T^{1/2}$ against $T^{-1/4}$ and from the linearity of the plot it is found that the results are in accordance with Mott's expression.

$$\sigma_1 = \frac{\sigma_0}{T^{1/2}} \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right] \quad (1)$$

$$\sigma_0 = 3e^2 \nu_{ph} \left[\frac{N(E_F)}{8\pi\alpha k}\right]^{1/2} \quad (2)$$

$$T_0 = \frac{\lambda\alpha^3}{kN(E_F)} \quad (3)$$

$$R = \left[\frac{9}{8\pi\alpha kTN(EW_F)}\right]^{1/4} \quad (4)$$

$$W = \frac{3}{4\pi R^3 N(E_F)} \quad (5)$$

where $N(E_F)$ is the density of states near the Fermi level, λ is a dimensionless constant (≈ 18), ν_{ph} is a frequency factor taken here as the Debye frequency ($\approx 3.3 \times 10^{12}$ Hz), α is the decay constant of the wave function of the localized states near the Fermi level, e is the electron charge and k is the Boltzmann constant. R is the mean hopping distance and W is the hopping energy.

In amorphous semiconductors, variable range hopping (VRH) conduction occurs at temperatures at which the phonons do not have sufficient energy for transfer to a nearest neighbour atom and the charge carrier hops from a neutral atom to another neutral atom situated at the same energy level which can be situated at many inter-atomic distances away.

The values of T_0 calculated from the slope of the $\log\sigma\, T^{1/2}$ against $T^{-1/4}$ curves for all the films as shown in Table I. The density of states near the Fermi level, $N(E_F)$, has been calculated using Equation 3, taking [50] $\alpha^{-1} = 1$ nm, and are given in Table I. It can be seen from this table that the value of $T_0 \sim 10^7$ K and density of states $N(E_F)$ is $\approx 10^{18}$ to 10^{20} cm^{-3} eV^{-1} which are in good agreement with the results reported by other workers [41, 46, 47, 51–53], for amorphous semiconductors. Assuming the same values of α as used for calculation of $N(E_F)$, it is possible to calculate the other two parameters for Mott's variable range hopping, namely, hopping distance R and hopping energy W, using Equations 4 and 5.

The values of R and W calculated at 100 K are given in Table I. The magnitudes of R and W are also quite reasonable for these materials. The product R is also

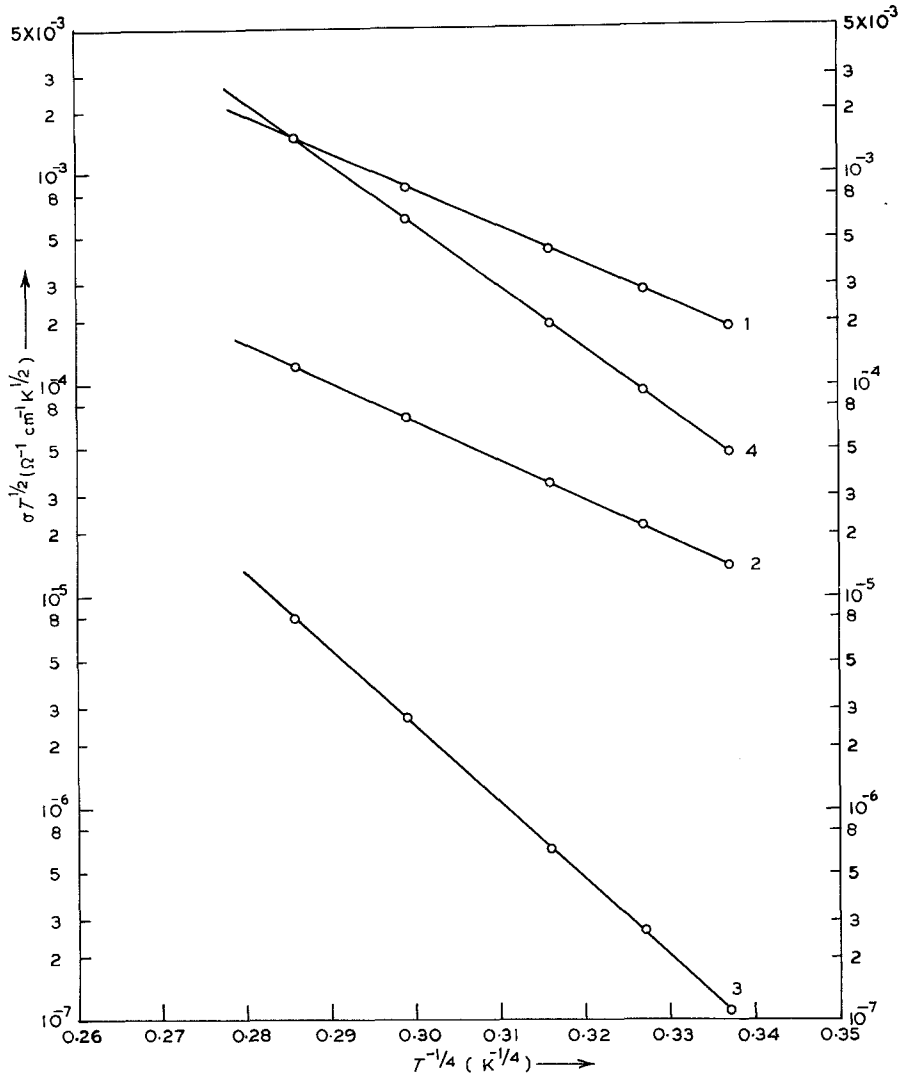

Figure 3 Variation of d.c. conductivity ($\log \sigma T^{1/2}$ against $T^{-1/4}$) as a function of $T^{-1/4}$ for the films shown in Fig. 2.

tabulated in Table I. For variable range hopping conduction in amorphous semiconductors, Mott proposed that $\alpha R \gg 1$ and $W \gg kT$. In the present case for all the films $\alpha R \gg 1$ and W is also $\gg kT$ at 100 K. It can be observed from Table I that the density of states near the Fermi level, $N(E_F)$, decreases with the increase of power density of the laser pulses up to 30 mJ cm^{-2}. It can also be seen from this table that the decrease in density of states improves the film quality thereby increasing the values of R and W. However, there is an increase in $N(E_F)$ and a decrease in the values of R and W in the films irradiated with laser pulses of energy density greater than 30 mJ cm^{-2}. This behaviour can be attributed to the transition of amorphous films into the polycrystalline state, which was also observed in electron diffraction studies on these films. It may also be mentioned that the value of α^{-1} ($\sim$ 1 nm) is also not strictly valid for the films irradiated with laser pulses of energy density more than 30 mJ cm^{-2}, as the films are no longer amorphous in nature. Moreover the values of $N(E_F)$ calculated from Mott's expression given in Equation 1 represent only a qualitative picture since Mott's theory is based on a number of assumptions of which the most important are: (i) energy independence of the density of states at E_F, (ii) neglect of the correlation effects in the tunnelling process, (iii) omission of the multi phonon process and (iv) neglect of electron–phonon interaction. However, in spite of these assumptions, one can draw a qualitative conclusion regarding the structure of the material.

The conductivity variation in the high temperature region (150 to 300 K) is taken as

$$\sigma_2 = \sigma_0' \exp\left(\frac{-\Delta E_1}{kT}\right) \quad (6)$$

where ΔE_1 is the conductivity activation energy and σ_0' is the pre-exponential factor.

The conductivity variation in the high temperature region cannot be attributed to the VRH process, as the

TABLE I

Film no.	Laser power density (mJ cm^{-2})	T_0(K)	$N(E_F)$ (eV^{-1} cm^{-3})	R at 100 K (10^{-7} cm)	αR at 100 K	W at 100 K (meV)	ΔE_1 (meV)	σ_0^1 (Ω^{-1} cm^{-1})
1	As-grown	2.51×10^6	8.32×10^{19}	4.72	4.73	27.70	69.35	1.56×10^{-2}
2	24	3.27×10^6	6.38×10^{19}	5.05	5.05	28.96	112.60	1.79×10^{-2}
3	30	4.73×10^7	4.41×10^{18}	9.85	9.85	56.64	128.00	4.71×10^{-3}
4	35	2.01×10^7	1.03×10^{11}	7.96	7.96	44.65	102.50	1.72×10^{-1}

values of ΔE_1 are much higher than the values of activation energy reported for the VRH process. The other conduction mechanism in the high temperature region can possibly be attributed either to the extended states conduction or to the localized states conduction at band edges. The values of the pre-exponential factor estimated for these films are much smaller than the values of σ_0' reported [54] for extended states conduction (100 to 500 $\Omega^{-1}\,cm^{-1}$). This suggests that the contribution of the extended states conduction is negligible.

The only probable conduction mechanism is conduction due to carriers in the localized states at the band edges [55, 56]. These small values of pre-exponential factor are mainly due to the low mobility of the carriers in the localized states at band edges.

4. Conclusions

Laser irradiation of a-Ge films, grown on glass, with laser pulses (10 to 50 $mJ\,cm^{-2}$, 20 nsec) causes significant changes in the conductivity values. The conductivity initially decreases with increase of laser power density up to 30 $mJ\,cm^{-2}$ but later increases rapidly with further increase of laser power. The d.c. conductivity increases with increase of temperature in the temperature range 77 to 300 K for the as-grown as well as laser-irradiated films. The conduction process in the low and high temperature regions can be attributed to the variable range hopping process and conduction in the localized states at the band edges, respectively.

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