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Effect of laser irradiation on structural, electrical and optical properties of SnO_2 films

A. L. DAWAR
Defence Science Centre, Metcalfe House, Delhi 110 054, India

A. KUMAR
Department of Physics, A. R. S. D. College, Dhaula Kuan, New Delhi 110 021, India

S. SHARMA, K. N. TRIPATHI, P. C. MATHUR
Department of Electronics Science, University of Delhi, South Campus, Benito Jaurez Marg, New Delhi 110 021, India

Thin films of SnO_2 were prepared using a spray pyrolysis technique. Films were irradiated with Nd:YAG laser pulses of various energy densities (2–50 mJ cm^{-2}) with varying number of pulses from 1–50. X-ray diffraction studies were made to investigate the structural changes due to laser irradiation. An improvement in crystallinity and an increase in grain size were observed in laser-irradiated films. Hall coefficient and Hall mobility studies were made in the temperature range 77–300 K for the as-grown as well as laser-irradiated films. An increase in mobility and a decrease in carrier concentration were observed in the films after laser irradiation. Optical transmission studies revealed that the refractive index increased as a result of laser irradiation.

1. Introduction

The laser processing of semiconductors has attracted considerable interest owing to its wide use in fabrication of integrated circuits [1–3], ohmic contacts [4], fabrication of p–n junctions [5–7] and silicide formation [8–10]. The process of laser irradiation using CW as well as pulsed lasers has been mainly confined to reactivation of the dopants and removal of lattice damage caused by ion implantation of the dopants [11–13]. Most of the work reported on laser processing has been confined to elemental semiconductors, particularly silicon. Although some problems arise in laser processing of some compound semiconductors due to the volatile nature of the elements present in them, this process can be used to improve the properties of specific materials such as GaAs [4], InSb [14], InP [15], CdTe [16], $Pb_{1-x}Sn_xTe$ [17], etc.

Studies of transparent and highly conducting oxide films have attracted the attention of many research workers because of their wide range of applications in electronic devices, namely solar cells, solar heat collectors, gas sensors, etc. The high transparency of tin oxide films in the visible region, together with their high reflectivity in the infrared, make them very attractive for use as transparent heat-reflecting material. The variation of the conductivity of SnO_2 layers in various ambient gases has been exploited for its use as gas sensors. Efforts have been made to improve the electrical and optical properties of SnO_2 films by annealing [18–23] them in different atmospheres such as air, vacuum, oxygen, forming gas (80% H_2 and 20% N_2), hydrogen, etc.

In the present work, thin films of SnO_2 were grown by the spray pyrolysis technique. Spray pyrolysis is the most widely used technique for the growth of large-area films because it is a simple and economical method for the production of thin films of oxidic materials. These films were then subjected to laser irradiation. Structural, electrical and optical properties of as-grown as well as laser-irradiated films were studied. An improvement in crystallinity and an increase in mobility have been observed in laser-irradiated films.

2. Experimental procedure

SnO_2 films were grown on pyrex glass substrates using the spray pyrolysis technique. The spray solution was prepared by dissolving $SnCl_2{:}2H_2O$ in HCl and diluted with propanol. A few drops of HNO_3 were added to the solution to enhance the oxidation. Oxygen was used as a carrier gas and flow rate was controlled using a flow meter. The substrate temperature was kept at 450 °C. This optimum temperature was chosen on the basis of previous studies [23].

The films were irradiated with laser pulses of various energy densities from 2–50 mJ cm^{-2} and by varying the number of pulses from 1–50 at a rate of 1 pulse s^{-1}. Laser pulses were of 20 ns width. The laser source used in the present investigations was a Nd:YAG laser of wavelength 1.06 μm. The diameter of the laser beam was about 5 mm.

X-ray diffraction studies were made on films grown on glass substrates using a Philips X-ray diffractometer (Model PW 1130/00). CuK_α radiation was used in these experiments and a 2θ spectrum from 15°–70° was recorded for as-grown as well as laser-irradiated films.

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The standard five-probe technique [24] was used to measure the Hall coefficient, R_H, and the d.c. conductivity. The ohmic nature of the contacts was confirmed throughout the temperature range by the linearity of the I–V characteristics. The sign of the Hall voltage showed that the samples were n-type.

Optical transmission studies were made on as-grown as well as laser-irradiated films grown on glass substrates using Hitachi 330-UV–VIS–NIR spectrometer.

3. Results and discussion

X-ray diffraction studies were made on the films grown on glass substrates to determine their structure and to identify the components and phases in the films. A typical diffraction spectrum for the as-grown SnO_2 film is shown in Fig. 1. The diffraction spectrum exhibits peaks at 2θ equal to 26.2°, 33.7°, 37.8°, 51.5°, 54.4°, 61.6° and 65.6° showing preferential growth of the film crystallites corresponding to (1 1 0), (1 0 1), (2 0 0), (2 1 1), (2 2 0), (3 1 0) and (3 0 1) planes, respectively. The results are in agreement with the standard ASTM data [25]. The predominent plane is (1 1 0). X-ray diffraction spectra for laser irradiated films at various energy densities are also shown in Fig. 1. The films irradiated with laser pulses show better orientation with (1 1 0) as the dominating plane. An increase in peak height corresponding to textural (1 1 0) growth and decrease in peak heights at (2 0 0) and (2 1 1) planes can be observed for laser-irradiated films as the energy density of laser pulses is increased. Typically, only one plane corresponding to (1 1 0) is observed for films irradiated with pulses of energy density 30 mJ cm^{-2}. It can be observed that the peak height corresponding to the (1 1 0) plane increases significantly with laser irradiation whereas the peak width decreases. This shows an improvement in the crystallinity and an increase in grain size of the laser-irradiated films. The grain size was determined from the X-ray diffraction data using

$$l = -\frac{\lambda}{D\cos\theta} \quad (1)$$

where l is the grain size, λ is the wavelength of the X-rays (0.154 nm) and D is the width of the peak at half maximum. The variation of grain size with energy density for films irradiated with 30 pulses is shown in Fig. 2. It can be seen that the grain size does not change for energy densities up to 10 mJ cm^{-2}. The increase in grain size is faster at higher energy densities. The increase in grain size with energy density can be attributed to the melting and recrystallization of the film surface. The film irradiated with pulses of energy density higher than 30 mJ cm^{-2} resulted in microcracks. Such type of effects may arise due to inherent non-uniform [26] energy distribution in the Q-switched laser beams.

Fig. 3 shows the variation of grain size with number of pulses for a typical energy density of 30 mJ cm^{-2}. It

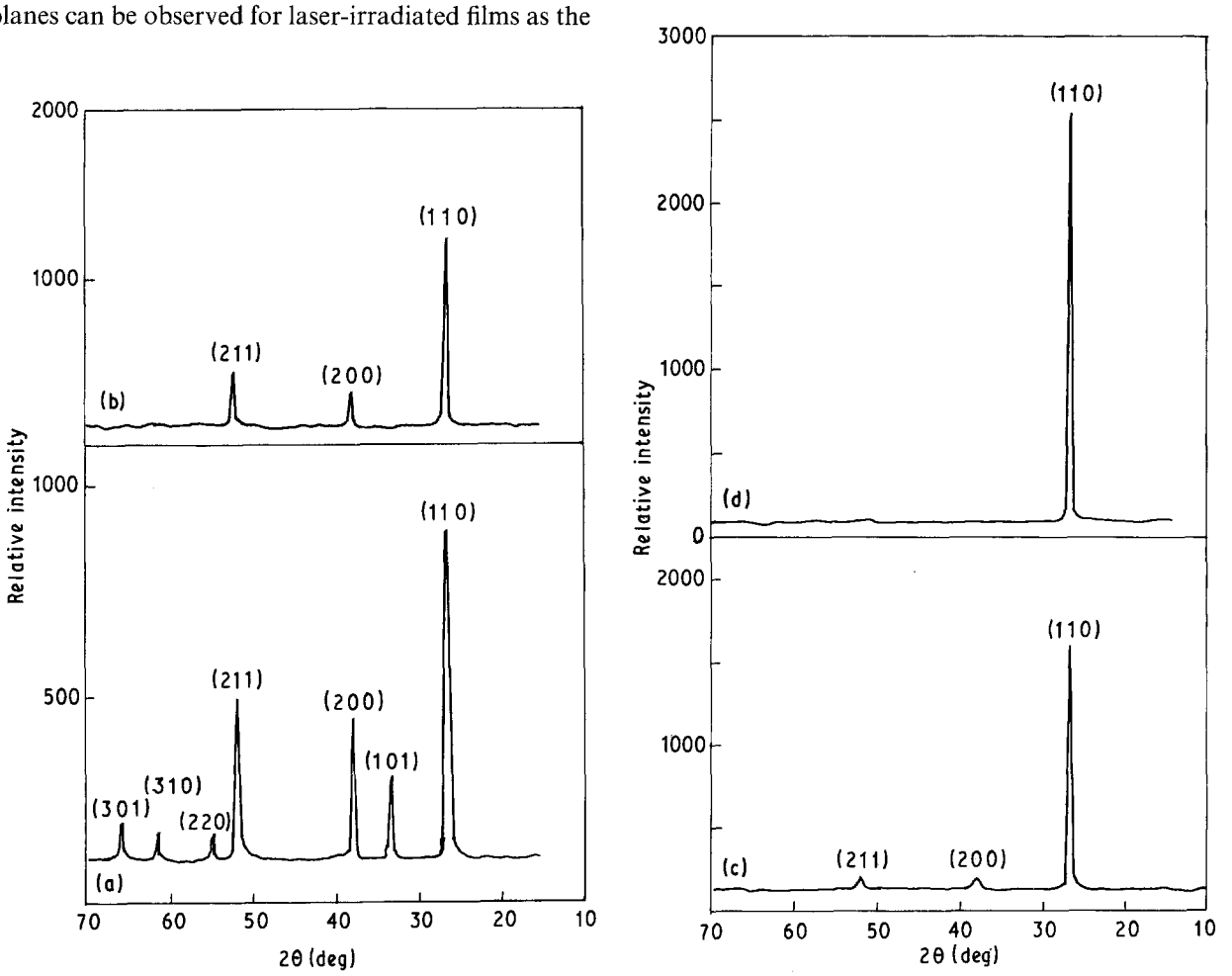

Figure 1 X-ray diffraction spectra of SnO_2 films: (a) as-grown film; (b) 10 mJ cm^{-2}, 30 pulses; (c) 20 mJ cm^{-2}, 30 pulses; (d) 30 mJ cm^{-2}, 30 pulses.

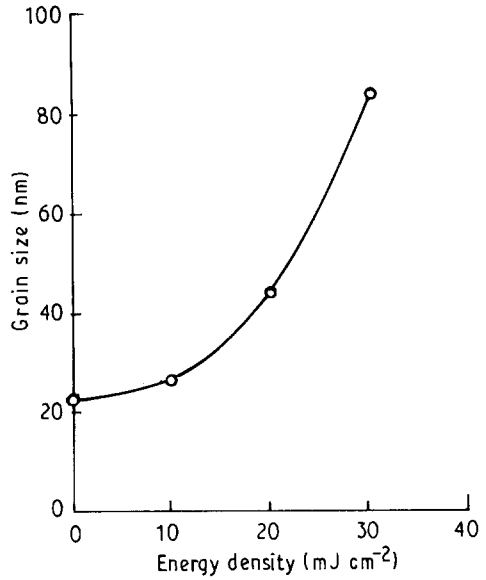

Figure 2 Variation of grain size with energy density for 30 pulses.

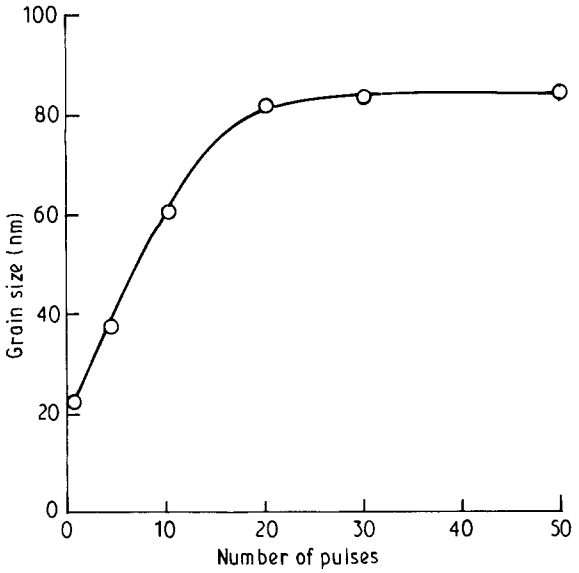

Figure 3 Variation of grain size with number of pulses for energy density 30 mJ cm^2.

can be observed that there is a significant increase in grain size with an increase in the number of pulses in the initial stages (typically up to 20 pulses) after which the grain size tends to saturate for higher number of pulses. This may be due to the fact that the repeated pulses more effectively remove spherical voids and microbubbles present in as-grown films. The change of structural properties after the cummulative effect of several pulses has also been observed by other workers [26–28]. Regolini *et al.* [28] suggested 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. 4 shows the variation of Hall coefficient, R_H, with energy density for a fixed number of pulses at 77 K. A similar trend was observed at 300 K also. The increase in R_H is slower for the lower energy densities and the increase is faster for the higher energy densities. The increase in R_H with the increase in energy density may be attributed to the decrease in defects.

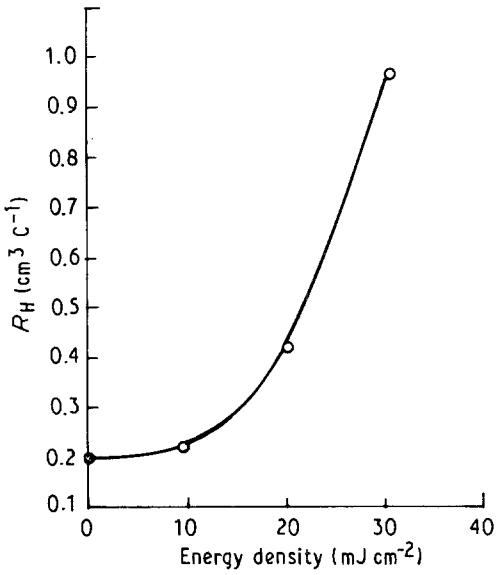

Figure 4 Variation of Hall coefficient, R_H, with energy density for 30 pulses at 77 K.

The variation of Hall coefficient, R_H, as a function of temperature for as-grown as well as laser-irradiated films for various energy densities is shown in Fig. 5. It can be seen that in as-grown films, R_H is almost independent of the temperature, indicating degeneracy. However, the value of R_H decreases as the temperature increases in the case of laser-irradiated films. The decrease in R_H is slower in the lower temperature region. This indicates that the carriers become thermally activated.

Fig. 6 shows a typical variation of Hall mobility, μ_H, as a function of temperature for as-grown films and films irradiated with laser at various energy densities. It may be observed that the value of Hall mobility increases with the increase of energy density. This increase in mobility with an increase in energy density could be due to the decrease in carrier concentration and increase in grain size. The irradiation with laser pulses also reduces the number of defects present in the films, thereby increasing the mobility. Further, it can be seen that the mobility decreases significantly

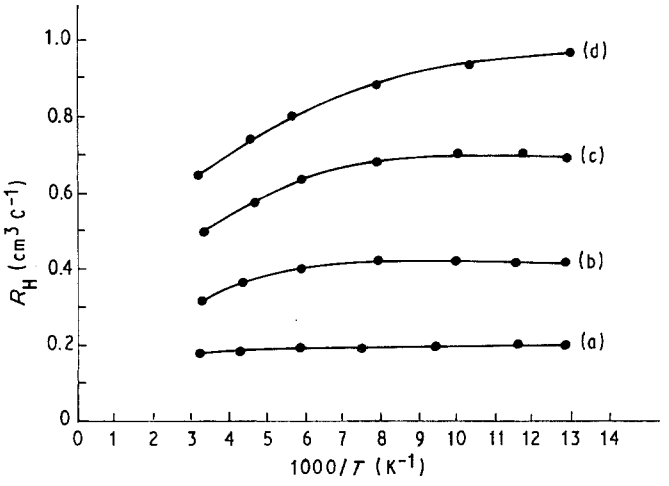

Figure 5 Variation of Hall coefficient, R_H, with temperature for various energy densites: (a) as-grown; (b) 20 mJ cm^{-2}, 30 pulses; (c) 25 mJ cm^{-2}, 30 pulses; (d) 30 mJ cm^{-2}, 30 pulses.

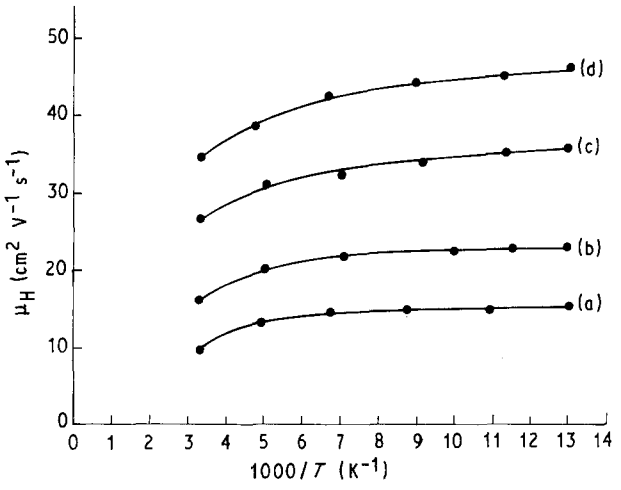

Figure 6 Variation of Hall mobility μ_H, with temperature for various energy densities: (a) as-grown; (b) 20 mJ cm^{-2}, 30 pulses; (c) 25 mJ cm^{-2}, 30 pulses; (d) 30 mJ cm^{-2}, 30 pulses.

with increasing temperature in the higher temperature region, indicating that the mobility is mainly limited by lattice scattering. In order to understand the scattering processes involved in the low-temperature region, the data have been analysed by plotting log μ_H versus log N curve as shown in Fig. 7. It can be observed that the mobility is a strong function of carrier concentration in accordance with the relation $\mu_H \alpha N^{-2/3}$. This mobility–carrier concentration relationship is found to be in good agreement with the Johnson and Lark Horovitz's theory [29] of ionized scattering for degenerate semiconductors. It confirms that, in the low-temperature region, the dominating scattering mechanism is due to ionized impurity centres. Islam and Hakim [30] as well as Imai [31] have also explained their results of thermoelectric power measurements in SnO_2 films as due to the presence of an ionized impurity scattering mechanism.

Optical transmission spectra were recorded for as-grown as well as laser-irradiated films. Typical curves of transmission versus wavelength are shown in Fig. 8

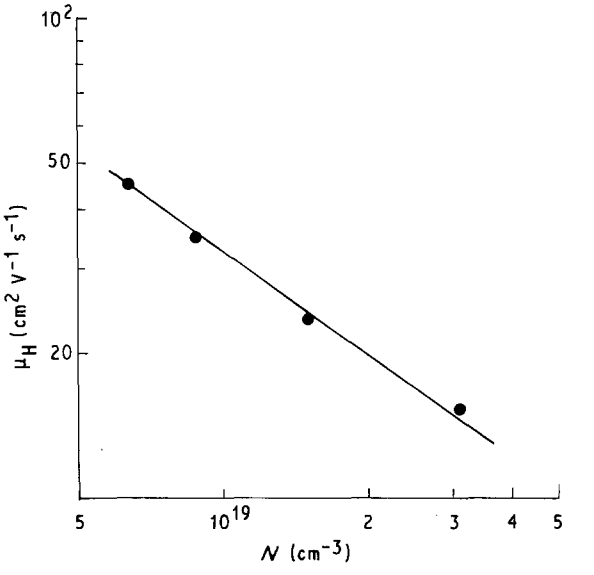

Figure 7 Variation of Hall mobility with carrier concentration (log μ_H versus log N).

for as-grown and laser-irradiated SnO_2 films. The absorption coefficient, α, was determined at various photon energies from optical transmission data using the relation

$$T = \exp(-\alpha t) \tag{2}$$

where t is the thickness of the film. The direct optical bandgap was estimated by plotting α^2 versus $h\nu$ in accordance with the relation

$$\alpha = \frac{c}{h\nu}(h\nu - E_0)^{1/2} \tag{3}$$

where E_0 is the optical bandgap and c is a constant. Fig. 9 shows the plot of α^2 versus $h\nu$ for as-grown as well as laser-irradiated SnO_2 films. The values of the optical band gap have been estimated by extrapolating the linear portion of the curves and are found to be 3.78 and 3.70 eV for as-grown and laser-irradiated films, respectively. The value of the band gap (3.78 eV) for as grown SnO_2 films agrees well with the reported data on undoped films [32, 33].

In order to calculate the value of refractive index and extinction coefficient, we have used the envelope method as suggested by Manifacier *et al.* [34]. The suitability of this method and comparison with other techniques has already been established in literature [35]. In the region of low absorption, the refractive index has been obtained from the interference maxima and minima using standard formulae.

$$n = [N_0 + (N_0^2 - n_0 n_1^2)^{1/2}]^{1/2} \tag{4}$$

where

$$N_0 = \frac{n_0^2 + n_1^2}{2} + 2n_0 n_1 \frac{T_{max} - T_{min}}{T_{max} T_{min}} \tag{5}$$

n_0 and n_1 are refractive indices of two transparent media (air and glass). The extinction coefficient, k, is obtained by solving the equation

$$A = \exp\left(\frac{-4\pi kt}{\lambda}\right) = \exp(\alpha t) \tag{6}$$

A is defined as

$$A = \frac{C_1[1 - (T_{max}/T_{min})^{1/2}]}{C_2[1 + (T_{max}/T_{min})^{1/2}]} \tag{7}$$

$$C_1 = (n + n_0)(n + n_1) \tag{8}$$

$$C_2 = (n - n_0)(n_1 - n) \tag{9}$$

The variation of refractive index with wavelength in the region 0.5–1.5 μm is shown in Fig. 10 for as-grown as well as laser-irradiated films. It can be observed that the value of refractive index is 1.77 and is nearly constant throughout the wavelength region studied. Similar behaviour of variation of n with wavelength has also been reported by other workers [32, 36] in this wavelength range. However, Melsheimer and Zifgler [37] have shown that there is dispersion in the wavelength range (300–800 nm), which is expected near the band edge. Although the behaviour of the n versus λ curve for laser-irradiated films is similar, the value of n increases to 1.84.

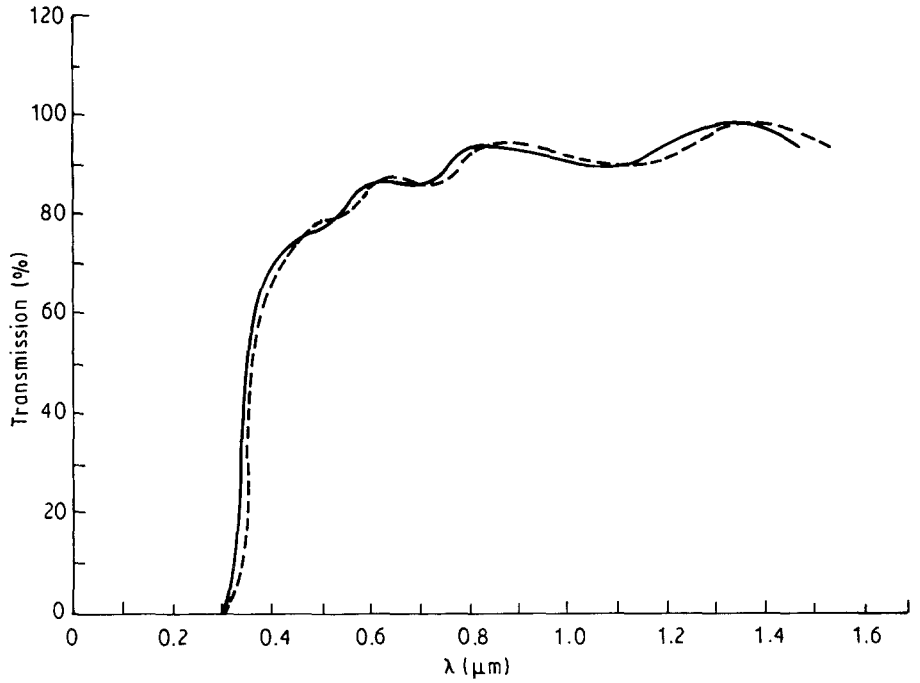

Figure 8 Transmission versus wavelength curves: (——) as-grown; (– – – –) 30 mJ cm^{-2}, 30 pulses.

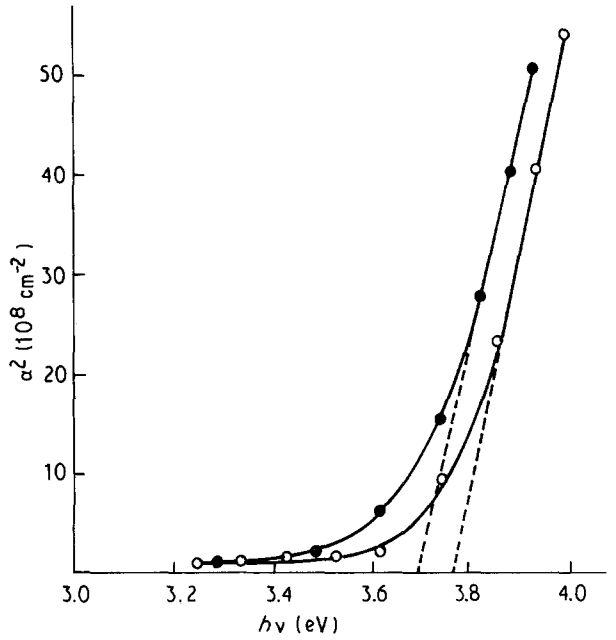

Figure 9 Variation of α^2 with photon energy, $h\nu$: (○) as-grown; (●) 30 mJ cm^{-2}, 30 pulses.

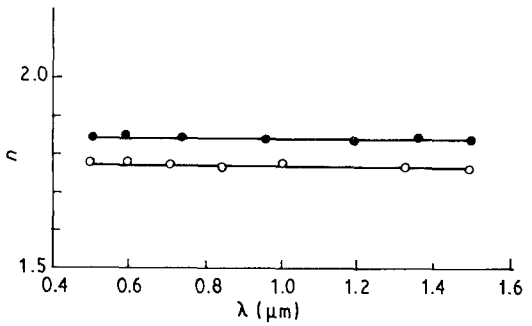

Figure 10 Variation of refractive index, n, with wavelength: (○) as-grown; (●) 30 mJ cm^{-2}, 30 pulses.

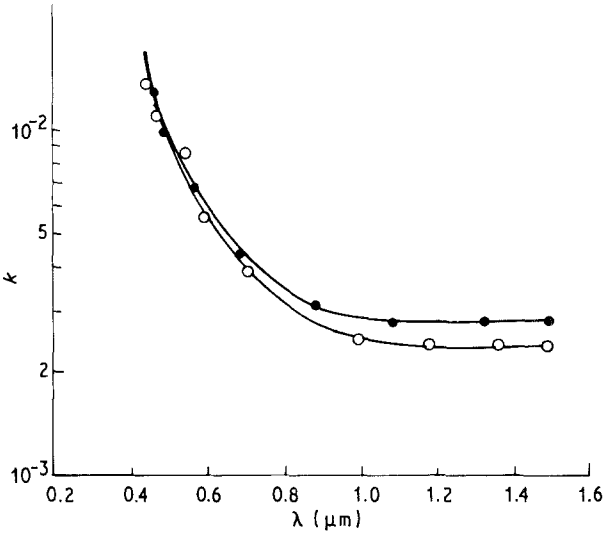

Figure 11 Variation of extinction coefficient, k, with wavelength for (○) as-grown; (●) 30 mJ cm^{-2}, 30 pulses.

The variation of extinction coefficient, k, with wavelength is shown in Fig. 11 for as-grown as well as laser-irradiated films. It can be observed that the value of k increases as the wavelength decreases. The increase in k in the lower wavelength range is associated with the fundamental bandgap absorption in the films.

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