Theoretical Approach to the Laser- Stimulated Luminescence in II-VI Semiconductor

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ABSTRACT

The present paper reports the laser mechanoluminescence (ML) in II-VI semiconductors. When a II-VI semiconductor exposed to laser pulse they will produce a shock-wave in the crystal and consequently the deformation of crystal takes place.

The rate of generation of electrons in the conduction band is given by

\[ g = \alpha_i n_i = \frac{2\alpha_i r_i \lambda N \text{BI}_0}{(\delta - \alpha)} \left[ \exp(-\alpha t) - \exp(-\delta t) \right] \]

For the laser-pulse of short duration the change in number of electrons in the conduction band

\[ \Delta n = \frac{2\alpha_i r_i \lambda N \text{BI}_0}{\delta(\beta - \alpha)} \left[ \exp(-\alpha t) - \exp(-\beta t) \right] \]

The maximum intensity and corresponding time is given by

\[ t_m_1 = \frac{1}{(\beta - \alpha)} \ln \left( \frac{\beta}{\alpha} \right) \quad \text{and} \quad I_m_1 = \frac{2\alpha_i r_i \lambda N \text{BI}_0}{\delta \beta} \]

Similarly we obtain the rate of generation of electron in the shallow traps and number of electrons in the shallow trap finally we obtain the maximum intensity and corresponding time as given

\[ t_m_2 = \frac{1}{(\alpha - \gamma)} \ln \left( \frac{\alpha}{\gamma} \right) \quad \text{and} \quad I_m_2 = \frac{2\eta \gamma \alpha_i \beta_i r_i \lambda N \text{BI}_0}{\delta(\beta - \alpha) \alpha} \]

The decay time of ML will be equal to the life time of electrons in the shallow traps.

Finally we obtain the ratio of \( I_m_2 \) and \( I_m_1 \) i.e.
The ratio \( \frac{I_{m_2}}{I_{m_1}} \) depend on the probability of transfer of electrons from the conduction band to shallow traps and on the ratio of pinning time of dislocation and life time of electrons in the shallow traps. By using laser pulse and an optical fiber the ML may be observed owing to the movement of single dislocation in II-VI semi-conductors.

Keywords: Mechanoluminescence, II-IV semiconductors.

INTRODUCTION

Luminescence induced during mechanical deformation of solids is known as mechanoluminescence (ML). ML links mechanical spectroscopic, electrical structural and other properties of solid. A large number of organic and inorganic solids exhibits the phenomenon of ML can excited by grinding, rubbing, cutting cleaving, compressing or by impulsive deformation of solids\(^{1-6}\). It can be excited by the thermal shocks produced during sudden cooling or heating of the solids. Primarily ML can be classified into two types : deformation ML and tribo ML. Deformation ML is produced during the deformation of solids and tribo ML is produced during the rubbing of two materials or during the separation of two materials or during the separation of two materials in contact. On the basis of the deformation in solids needed for producing ML, deformation ML can further be subdivided into three types namely, elastico ML, plastico ML and fracto ML. The ML occurring during elastic deformation of solids is called elastico deformation of solids is called elastico ML, and the ML occurring during fracture of solids is called fracto ML.

We have been interested whether ML could be made to occur using a high energy laser pulses as the stress inducing agent\(^7\). The present paper reports the theory of laser ML in II-VI semiconductors. In analogy with the laser thermo luminescence the ML caused by the deformation owing to laser pulses may be called as laser ML. The others materials like elemental and III-V semiconductors exhibit ML, during their fracture, which is not related to the movement of dislocations hence laser ML in this semiconductors may be observed during only when intense laser shocks pulses instead of laser will create crakes in this semiconductor as such theory of laser ML in these semiconductors may be quite different from that of II-VI semiconductors whereby intense ML is observed during the movement of dislocations in these semiconductors.
THEORY

An analysis of the possible ML mechanisms has shown that the interacting between charged dislocations and activator centers leads to activator ionization. Ionization may occur by tunneling of electrons from the impurity level of the conduction band close to a charged dislocation \(^{8-11}\). The electric field at a distance \(r\) from the core of a charged dislocation is given by \(E = 2q/\varepsilon_0 r\), where \(q\) is the linear charge density of dislocation, \(\varepsilon_0\) is the dielectric permittivity. At \(q = 0.35\) e/units, where \(e\) is the electronic charge, the electric field at a distance \(r = 10^{-7}\) cm from the dislocation core is \(E = 3.4 \times 10^6\) volt/cm\(^2\). In this case, the electric field due to charged dislocations ionizes the electrons from filled traps and the subsequent recombination of electrons with the activator centers containing holes gives rise to luminescence. The process can be represented as follows:

\[
L + d \longrightarrow L^+ + e + D
\]

\[
A(P) + e \longrightarrow A \longrightarrow A + h\nu
\]

where \(L\) is a trap filled with electron, \(L^+\) is an empty trap and \(A(P)\) is the activator containing hole.

Supposing a II-VI semiconductor like ZnS is exposed to an infrared laser pulse whose intensity is given by \(I = I_0 \exp(-\delta t)\), where \(I_0\) is the intensity at \(t = 0\) and \(\delta\) is a factor inversely related to the pulse duration of laser. It is known that the laser pulse produces a shock-wave in the crystal and consequently the deformation of crystal takes place\(^{12-14}\). For a laser pulse of short duration and low pulse energy, the local heating will not be significant and consequently the intensity of black body radiation may be assumed to be negligible as compared to that of the laser ML produced in the bulk of crystal. It is to be noted II-VI semiconductors exhibit ML even during their plastic deformation.

Let us assume that the time dependence of the rate of generation \(\frac{a}{b}\) of moving dislocations in the localized region of the crystal due to the laser pulse is given by

\[
g_d = BI_0 \exp(-\delta t)
\]

where \(B\) is correlating factor between \(g_d\) and the intensity of the laser pulse.

If \(r_i\) is the radius of interaction between moving dislocations and the filled traps in the crystal and \(\lambda\) is the mean distance traveled by a dislocation before its pinning, then the volume in which \(g_d\) dislocation of unit length can interact per unit time will be \(2r_i\lambda g_d\).

If \(N_t\) is the concentration of filled traps, then the number of filled traps interacting with the dislocation per unit time is given by

\[
g_i = 2r_i\lambda g_d N_t
\]

From eqs. (1) and (2), we get

\[
g_i = 2r_i\lambda N_t BI_0 \exp(-\delta t)
\]
If $\alpha_1$ is the rate constant for tunneling of electrons from the filled traps to the conduction band and $\alpha_2$ is the rate constant for the dropping back of the trapped electrons, then we may write the following rate equation –

$$\frac{dn_i}{dt} = g_i - (\alpha_1 + \alpha_2)n_i$$

or

$$\frac{dn_i}{dt} = g_i - \alpha n_i$$

(4)

where $g_i$ is the number of interacting filled traps at any time $t$ and

$$\tau_p = 1/(\alpha_1 + \alpha_2) = \frac{1}{\alpha}$$

is the lifetime of interacting filled traps or the pinning time of dislocations.$^{15}$

From eqs. (3) and (4), we get

$$\frac{dn_i}{dt} = 2r_i \Lambda N_i B I_o \exp(-\delta t) - \alpha n_i$$

(5)

Integrating eqs. (5) and taking $n_i = 0$ at $t = 0$, we get

$$n_i = \frac{2r_i \Lambda N_i B I_o}{(\delta - \alpha)} \left[ \exp(-\alpha t) - \exp(-\delta t) \right]$$

(6)

Thus the rate of generation of electrons in the conduction band may be given by

$$g = \alpha_i n_i = \frac{2\alpha_i r_i \Lambda N_i B I_o}{(\delta - \alpha)} \left[ \exp(-\alpha t) - \exp(-\delta t) \right]$$

(7)

If $\beta_1$ and $\beta_2$ are the rate constants for the radiative and non-radiative recombination of electrons with the hole centers, respectively, and $\beta_2$ is the rate constants for the transfer of electrons to the shallow traps, then we may write the following rate equation.

$$\frac{d(\Delta n)}{dt} = g - (\beta_1 + \beta_2 + \beta_3)\Delta n$$

or

$$\frac{d(\Delta n)}{dt} = \frac{2\alpha_i r_i \Lambda N_i B I_o}{(\delta - \alpha)} \left[ \exp(-\alpha t) - \exp(-\delta t) \right] - \beta \Delta n,$$

(8)

where $\Delta n$ is the change in the number of electrons in the conduction band at any time $t$. $\beta = (\beta_1 + \beta_2 + \beta_3)$ and $1/\beta = \tau$, is the lifetime of electrons in the conduction band.

Integrating eq. (8) and taking $\Delta n = 0$ at $t = 0$, we get

$$\Delta n = \frac{2\alpha_i r_i \Lambda N_i B I_o}{(\delta - \alpha)} \left[ \frac{\exp(-\alpha t)}{(\beta - \alpha)} - \frac{\exp(-\delta t)}{(\beta - \alpha)} \right]$$

(9)

For a laser-pulse of short duration, $\delta \gg \beta$ and $\delta \gg \beta$, and in the deformation region $\beta > \alpha$. Thus, eq. (9) may be expressed as

$$\Delta n = \frac{2\alpha_i r_i \Lambda N_i B I_o}{\delta(\delta - \alpha)} \left[ \exp(-\alpha t) - \exp(-\delta t) \right]$$

(10)

Thus, the intensity of transient ML may be given by

$$I_1 = \beta_1 \Delta n = \frac{2\alpha_i r_i \Lambda N_i B I_o}{\delta(\delta - \alpha)} \left[ \exp(-\alpha t) - \exp(-\beta t) \right]$$

(11)
Equation (11) indicates that the ML intensity should attain a maximum value $I_{m1}$ for a particular value of time $t_{m1}$. For $\beta > \alpha$ using eq. (11) $t_{m1}$ and $I_{m1}$ may be given by

$$t_{m1} = \frac{1}{(\beta - \alpha)} \ln \left( \frac{\beta}{\alpha} \right)$$

and

$$I_{m1} = \frac{2\alpha_1\beta_1 r I N_1 B I_o}{\delta \beta}$$

As $\beta >> \alpha$ for $\beta t >> t$ eq. (11) be expressed as

$$a
\begin{cases}
\frac{\Delta n}{\delta}
\end{cases}$$

Equation (14) indicates the exponential decay of ML intensity $I_1$ in which the decay time of ML will give the lifetime of interacting filled traps or the pinning time of dislocations.

For $\beta >> 1$ eq. (10) may be expressed as

$$\Delta n = \frac{2\alpha_1 r I N_1 B I_o}{\delta (\beta - \alpha)} \exp(-\alpha t)$$

Thus, the rate of generation of electrons in shallow traps may be given by

$$G = \beta_3 \Delta n = \frac{2\alpha_1 r I N_1 B I_o}{\delta (\beta - \alpha)} \exp(-\alpha t)$$

If $\tau_s$ is the lifetime of electrons in the shallow traps, then we may write the following rate equation

$$\frac{d\Delta n_s}{dt} = \frac{2\alpha_1 r I N_1 B I_o}{\delta (\beta - \alpha)} \exp(-\alpha t) - \gamma \Delta n_s$$

where $\Delta n_s$ is the number of electrons in the shallow traps at any time $t$, and

$$\tau_s = \frac{2\alpha_1 r I N_1 B I_o}{\delta (\beta - \alpha)(\alpha - \gamma)} [\exp(-\gamma t) - \exp(-\alpha t)]$$

Integrating eq. (17) and taking $n_s = 0$, at $t=0$, we get

$$\Delta n_s = \frac{2\alpha_1 r I N_1 B I_o}{\delta (\beta - \alpha)(\alpha - \gamma)} [\exp(-\gamma t) - \exp(-\alpha t)]$$

If $\frac{a}{b}$ is the probability of radiative recombination of electrons released from the shallow traps, then the intensity $I_2$ of the delayed ML may be given by

$$I_2 = \eta \Delta n_s \gamma$$

$$= \frac{2\eta \gamma \alpha_1 r I N_1 B I_o}{\delta (\beta - \alpha)(\alpha - \gamma)} [\exp(-\gamma t) - \exp(-\alpha t)]$$

The above equation indicates that the intensity of delayed ML should attain a maximum value $I_{m2}$ for a particular value of time $t_{m2}$. For $\alpha > \gamma$, using ed. (19), $t_{m2}$ and $I_{m2}$ may be given by

$$t_{m2} = \frac{1}{(\alpha - \gamma)} \ln \left[ \frac{\alpha}{\gamma} \right]$$

and,

$$I_{m2} = \frac{2\eta \gamma \alpha_1 r I N_1 B I_o}{\delta (\beta - \alpha)(\alpha - \gamma)} [\exp(-\gamma t) - \exp(-\alpha t)]$$
As $\alpha > \gamma$, for $\alpha t >> 1$, from eq. (19) the decay of ML intensity $I_2$ may be given by

$$I_{d2} = \frac{2n\gamma\alpha \beta_3 t \lambda N \beta_1 \exp \left( \frac{-\gamma}{\tau_s} \right)}{\delta (\beta - \alpha) (\alpha - \gamma)}$$  \hspace{1cm} (22)

Equation (22) indicates the exponential decay of ML intensity $I_2$, in which the decay time of ML will be equal to the life time of electrons in the shallow-traps. As $\frac{a}{b}$ and $\frac{a}{b}$, from eqs. (13) and (22), the ratio of $I_{m2}$ and $I_{ml}$ is given by

$$\frac{I_{m2}}{I_{ml}} = \frac{\beta_3 \gamma}{\beta \alpha} = \frac{Pt}{\tau_s} \tau_p$$  \hspace{1cm} (23)

where $\frac{Pt}{\beta} = \frac{\beta_3}{\beta}$ is the probability of transfer of electrons from the conduction band to shallow traps.

The above equation shows that the ratio $I_{m2} / I_{ml}$ should depend on the probability of transfer of electrons from the conduction band to the shallow traps and on the ratio of pinning time of dislocation and the lifetime electrons in the shallow traps.

**EXPERIMENTAL SUPPORT**

We are able to induce luminescence in several non-coloured organic and inorganic crystals by a 20 ns, 1060 nm pulse from a Nd glass laser whose pulse energy varied from 0.5 to 4 J cm$^{-2}$ (≈ 200MW peak power). The spectra of laser induced emission were obtained by using a silicon intensified (SIT) vidicon detector and a multichannel analyzer. So far as the time dependence of ML in II-VI semiconductors is concerned our preliminary observations have shown the occurrence of two ML peaks. This needs a further detailed investigation.

**CONCLUSIONS**

The importance conclusions drawn from the present investigation are as given below:

(i) When the ML in a II-VI semiconductor will be excited by the deformation caused by a laser pulse, then the ML intensity versus time curve should possess two peaks, where the first peak should occur in the region where deformation takes place owing to laser pulse and the second peak should occur in the post-deformation region.

(ii) The decay time of ML after $t_{ml}$ should give the pinning time of dislocations and the decay time of ML after $t_{m2}$ should give the lifetime of electrons in the shallow traps.

(iii) The ratio $I_{m2} / I_{ml}$ should be given by the product of probability of transfer of electrons from conduction band to shallow traps and the ratio of pinning time of dislocations and the lifetime of electrons in shallow traps.

(iv) By using laser pulse and an optical fiber, the ML may be observed owing to the movement of a single dislocation in II-VI semiconductors.
REFERENCES