Jahn-Teller Effect in Diamond-like Carbon

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Abstract

The Jahn-Teller effect used semi-theoretically to analyse UV-visible spectra of the diamond like-carbon films on Si substrates. By deconvolution of UV-visible absorption spectra of the typical films, different absorption lines found. For each sample, six lines which were related to $V^\circ$ by Jahn-Teller effect are distinguished. Our theoretical approach based on distortion of the $V^\circ$ as the consequence of the stress in the films, is in agreement with experimental results. The shift of the Jahn-Teller lines toward the zero phonon line of $V^\circ$ were found in accordance to stress decrease in the films. The difference between room temperature and low temperature spectra is discussed. We found that the splitting of the excited state of $V^\circ$ in the films under stress is twice as large as that of the ground state.

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I. INTRODUCTION

There is a growing interest in vacancies and vacancy related effects in DLC, a-C and a-C:H films from theoretical and experimental points of view. Despite large improvement in the preparation techniques for these type of films, a large number of vacancies is present in such films [1]. This is due to the nature of preparation since practically it is not possible to make films free of vacancies.

Different varieties of vacancies exist in these films but the main ones are neutral-single vacancy $V^\circ$, one carbon with its four valance electrons is missing, and negatively charged-single vacancy $V^-$, one carbon with its three valance electrons is missing. Such vacancies exist in natural diamond or are made in it by neutron, electron or gamma bombardment [2–4]. These vacancies have peculiar absorption, photoluminescence (PL) and cathodluminescence (CL) emission. All the PL, CL and absorption spectra show many feature, including different peaks and shoulders [5–8]. The GR1 band with zero phonon line at 1.673 eV and ND1 with zero phonon line at 3.149 eV are associated with $V^\circ$ [9] and $V^-$ [10], respectively.

Much work is done on the effect of uniaxial stress in natural diamond to explain lines of GR1 band [11,12,13]. It is reported that for films there is a strong correlation between PL intensity and stress [11] and also, between the line-width of zero phonon line and film strain [13,14].

In recent years, considerable attention has been paid to the degenerate electron-lattice interaction in molecules and defect centres in solids, called Jahn-Teller effect (JTE) [16,17,18].

In this paper JTE is used phenomenologically to explain our experimental results on absorption spectra of DLC film on silicon substrate. The nature of stress in films and its distortion effect is explained. The electronic states splitting of $V^\circ$ under stress are obtained. The relative intensity change of room temperature spectra to that of low temperature spectra also is explained.

II. EXPERIMENT

DLC films were made from liquid gas (60% Butane and 40% Propane) on 10 × 20 × 1mm silicon substrates. The growth conditions were:
Gas pressure: $85 \times 10^{-3}$ Torr
Substrate temperature: 200°C
Direct voltage: 450 V
Deposition time: different for different samples.
Different deposition time means different thickness of films. The absorption of the films were measured by double beams spectrometer at room temperature and in the reflection mode.

The absorption spectra of typical films in UV-visible region (200-1200 nm) are shown in Fig. 1. As it is evident from this figure the absorption peaks are at different wavelength for different samples. They have moved in accordance to the deposition time of growth, showing that the peak displacement depends on thickness. The spectra were deconvoluted.
FIG. 1. Room temperature UV-visible spectra of films deposited at 85 mtorr and 200°C for samples (Si21) 1 hour, (Si22) 2.5 hour, (Si25) 2 hour, and (Si26) 4 hour on Si-substrates.

FIG. 2. Gaussian deconvolution of UV-visible spectra of "Si21", "Si22", "Si25" and "Si26". For each sample, curve by ___ show the experimental spectra, curves by ___ show the unrelated lines and curves by ___ show the Jahn-Teller lines.

by normalized Gaussian with accuracy better than 99.95%. The resultant deconvolution for mentioned samples are shown in Fig. [I].

Some of these lines which were found by deconvolution, had been reported before and some had not [1, 5, 8, 11–13, 15, 18]. We will come to this point later.

III. JAHN-TELLER EFFECT

In V° vacancy of diamond structure there are four sp$^3$ electrons rigidly connected to the atoms surrounding the empty space of the vacant atom. Hence, there is a molecule with four atoms, each with one sp$^3$ electron sitting at the A, B, C, and D corners of the cubic unit cell of the diamond structure as shown in Fig. [III].

Degenerate electron state of nonlinear molecule such as V° and V− as stated by Jahn and Teller [19] are not stable and the degeneracy of these molecules have to be removed or reduced for stability. With no distortion, such a molecule has all the symmetry of the diamond structure except the translational symmetry. The point symmetry of the diamond lattice is T$_d$. The one electron states of this molecule have $a_1$ and $t_2$ symmetry. With those sp$^3$ shown in Fig. [III], we have
FIG. 3. $V^\circ$ vacancy of diamond structure. Each sp$^3$ electron are sited in A, B, C and D corners.

$$a_1 = \frac{1}{2} [\psi_A + \psi_B + \psi_C + \psi_D]$$
$$t_{2x} = \frac{1}{2} [\psi_A - \psi_B + \psi_C - \psi_D]$$
$$t_{2y} = \frac{1}{2} [\psi_A - \psi_B - \psi_C + \psi_D]$$
$$t_{2z} = \frac{1}{2} [\psi_A + \psi_B - \psi_C - \psi_D].$$

(1)

where $\psi_i$ is sp$^3$ wave function at $i$th site. The degenerate electron states correspond to the representations E, $T_1$ and $T_2$ of this group.

In this molecule electron-electron correlation leads to a multiple structure with $^1E(a_1^2t_2^2)$ being the lowest energy state observed for $V^\circ$. Transition to the state $^1T_2(a_1^2t_2^2)$ is then associated with GR1 \cite{9}.

The ground state, $^1E$ and the first excited state, $^1T_2$ of this molecule have two and three fold symmetry, respectively. Therefore, GR1 bond is sum of six transition lines. Under a distortion such as stress, the symmetry of this molecule will be broken, hence, the degeneracy of the levels will be resolved and there will be five splitted levels, two for ground state, $^1E$, and three for exited state, $^1T_2$:

$$E \rightarrow E \pm \alpha,$$
$$T \rightarrow T \pm \beta, T + 2\beta$$

(2)

where E and T are the energies of $^1E$ and $^1T_2$ levels, respectively \cite{20}. With such splitted levels, there are six transitions as shown in Fig. \[11\].

The energies for this transitions are;

$$(T - E) + (2\beta + \alpha), (T - E) + (2\beta - \alpha),$$
$$(T - E) + (\beta + \alpha), (T - E) + (\beta - \alpha),$$
$$(T - E) + (-\beta + \alpha), (T - E) + (-\beta - \alpha).$$

(3)

Using the experimental information of any two lines, one is able to calculate $\alpha$ and $\beta$. Then using $\alpha$ and $\beta$ so obtained, the transition energy of four other lines could be predicted in this approach.
IV. THEORETICAL RESULTS

As it is apparent from deconvolution result of each sample, there are two lines very close to each other, namely 513 and 514 nm lines for "Si21", 583 and 586 nm lines for "Si22", 574 and 576 nm lines for "Si25" and 612 and 615 nm for "Si26". The only rational possibility for this to happen is the case when the transition energy of \( E - \alpha \rightarrow T + \beta \) is very close to the transition energy of \( E + \alpha \rightarrow T + 2\beta \). In this case \( \beta = 2\alpha \). Physically this means that the splitting of the exited state is twice the splitting of the ground state.

\( (T - E) \) is the transition energy of non-disturbed \( V^\circ \) which is 1.673 eV. Using this value and the experimental resultant explained above, \( \alpha \) and \( \beta \) are calculated for each sample. Inserting the obtained values of \( \alpha \) and \( \beta \) in Eqs. (3), the Jahn-Teller transition lines for each sample were predicted. These results are summarized in Table I.

V. DISCUSSION

In process of making the film, two different stages can be distinguished. In the first stage, deposition starts as islands at different points on substrate and at different times. At the second stage, these islands grow and reach each other and then the film grows as a film. At the early stage of the film growing process, there are mis-matchings in domain walls of islands and also, interface of film and substrate. Such mis-matching produce strong stress in the film. This stress causes the symmetry breaking and splitting of the energy levels.

As the film thickness increases, the effect of the bulk will prevail and only the stress in the interface will be strong. Therefore the resultant stress in the film decreases, and consequently the effects related to stress such as energy levels splitting decrease. Figures (4[1]) and (4[2]) are evidences for this effect. As the deposition time increases, meaning that the thickness increases, the JT related lines move toward zero-phonon line of \( V^\circ \), 741 nm, Fig [V]. In Table I theoretical and experimental wavelengths of the JT related lines are compared. The last row shows the good agreement between experiment and our theoretical approach.

Another important point which deserves attention, is the relative intensity of the two
TABLE I. Theoretical and experimental values, first row sample no., second row is deposition time (D.T.) in hour, third row is theoretical energy (T.E.), forth row is theoretical calculated wavelength (T.W.), fifth row is experimental wavelength, sixth row is Jahn-Teller lines assigned to GR1 band (JTLGR1) and last row is relative error.

| Sample | Si21 | Si22 |
|--------|------|------|
| D.T. (hour) | 1.0  | 2.5  |
| α (eV) | 0.246 | 0.149 |
| T.E. (eV) | 2.90 2.41 1.92 1.43 0.93 | 2.42 2.12 2.12 1.82 1.52 1.23 |
| T.W. (nm) | 427 514 646 869 1327 | 513 585 585 681 814 1011 |
| E.W. (nm) | 409 513 515 653 885 1227 | 517 582 587 673 814 1020 |
| JTLGR1 | GR1a GR1b GR1c GR1d GR1e GR1f | GR1a GR1b GR1c GR1d GR1e GR1f |
| % Error | 4.10 0.16 0.16 1.12 1.84 7.57 | 0.86 0.26 0.26 0.13 0.00 1.00 |

| Sample | Si25 | Si26 |
|--------|------|------|
| D.T. (hour) | 2.0  | 4.0  |
| α (eV) | 0.161 | 0.116 |
| T.E. (eV) | 2.48 2.16 2.16 1.83 1.51 1.19 | 2.25 2.02 2.02 1.79 1.56 1.33 |
| T.W. (nm) | 500 575 575 676 820 1042 | 551 614 614 693 796 935 |
| E.W. (nm) | 514 574 576 671 823 1097 | 523 613 615 697 804 970 |
| JTLGR1 | GR1a GR1b GR1c GR1d GR1e GR1f | GR1a GR1b GR1c GR1d GR1e GR1f |
| % Error | 2.76 0.17 0.17 0.81 0.35 5.23 | 5.03 0.23 0.23 0.55 1.03 3.77 |

FIG. 5. Shift of Jahn-Teller lines toward zero phone line of V°, dash line 741 nm, where □ GR1a, ★ GR1b and GR1c, + GR1d, ● GR1e and * GR1f are.
lines with equal energy. One of these lines is the transition from lower level of the ground state, and the other is the transition from the higher level of the ground state, which is thermally less populated than the first one.

Up to now, in addition to our results, many lines are reported by different groups on irradiated and non-irradiated natural diamond and carbon films. Similar to ours some of these lines are related to vacancies under stress. In low-temperature, the transitions from upper ground state are weak. In PL and CL also the related transitions to the lower ground state are small.

VI. CONCLUSION

Upon deconvolution of UV-visible spectra many hidden lines appeared which we considered them for analysis of the spectra. Those non apparent lines are not the less important ones.

We believe the lines seen at different wavelengths in our results and others are due to the vacancy based on JTE. The strength of the effect depends on the growth conditions and thickness of the films.

The results of our phenomenological approach are in good agreement with our experimental results. Therefore, this approach could be used to analyse the physical properties of carbon films.

First excited state splitting of $V^\circ$ in the films under stress is two times of ground state splitting in contrast to some theoretical models [13].
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