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Thermally stimulated current in the absence of optical excitation in the annealing of tetracene and pentacene films

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Thermally stimulated current (TSC) occurring without optical excitation was observed in the annealing of fresh tetracene and pentacene films deposited at low temperatures in the dark. The agreement between the experimental and theoretical profiles of the TSC showed that the TSC is caused by trapped charge-transfer excitons. It was concluded that the charge-transfer state was probably excited by energy transfer due to a phase transformation.

I. INTRODUCTION

It is well known that linear polyacenes, such as anthracene and tetracene, form amorphous films when they are deposited at low temperatures. Evidence for this is as follows: the lack of Davydov splitting in the absorption spectra;[1,2] the existence of diffused patterns in x-ray[3] and electron diffraction;[4] and a dark view under a polarizing microscope observed with crossed Nicol prisms. These were usually observed at room temperature, after the films that were deposited at low temperatures were heated.

Recently, absorption spectra of amorphous polyacene films were measured as a function of the annealing temperature.[5-7] Upon warming the amorphous films formed at low temperatures, an irreversible change in the spectra was detected. *In situ* electron diffraction studies of grown films of tetracene and pentacene were reported by Eiermann *et al.*[8] They showed that some discontinuity in the d spacing occurred at the film formation temperature. The former suggests that the electronic state of fresh amorphous films changes in the intermediate stage of annealing, while the latter suggests a crystal structural change.

A thermally stimulated current (TSC) without optical excitation during annealing, which seems to be correlated with these effects, was observed in anthracene, tetracene, and pentacene films. These films were deposited at low temperatures on substrates on which surface-type electrodes were previously formed by deposition. In general, during a TSC measurement, the traps in a solid specimen must be filled by optical excitation at low temperatures. The temperature of the specimen is then raised at a constant rate, resulting in the freeing of carriers. The liberated carriers contribute to an excess current under an applied field, namely, the TSC. Therefore, the appearance of the TSC without optical excitation suggests that a mechanism for the electronic excitation exists in the formation or the annealing of linear polyacene films deposited at low temperatures. In this paper a study of the TSC without optical excitation occurring when tetrancene and pentacene films are deposited at temperatures between 153 and 203 K is made.

II. EXPERIMENTAL PROCEDURE AND RESULTS

A. Tetracene

A synthesized quartz plate was used as the substrate with Au being deposited on the quartz plate to form comb-type electrodes. The electrode separation was 1 mm. The substrate was attached to a temperature-controlled Cu block placed in a vacuum cryostat. After being kept at 373 K for one hour in 2×10^{-5} Torr vacuum, it was allowed to cool. The temperature of the substrate was monitored by thermocouples attached to the surfaces of the substrate and the Cu block. The temperature dependence of the surface leak current in the substrate was measured under a bias voltage of 850 V, applied by dry batteries. No definite TSC signals were observed, as is shown in Fig. 1(a). After the substrate was further cooled, tetracene refined through sublimation was then deposited on the same substrate at a low tempera-

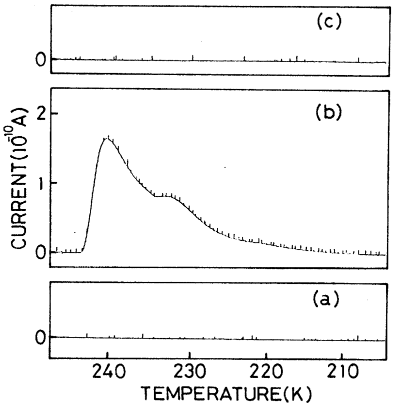

FIG. 1. An example of the TSC occurring in a tetracene film. Conditions of the film formation are as follows: thickness, 13×10^2 Å; deposition rate, 14 Å/s; T_f, 173 K. (a), (b), and (c) are current measured as a function of temperature for the substrate, the film in measurement I, and that in measurement II, respectively.

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ture T_f under short-circuiting of the electrodes. The deposition rate, from 3 to 16 Å/s, and the film thickness, from 5×10^2 to 33×10^2 Å, were measured by a film thickness monitor and a multireflection interferometer, respectively. The bias voltage was applied to the film after deposition. The temperature dependence of the current through the film was then measured, also at a heating rate between 0.04 and 0.06 K/s in the absence of light (measurement I). This time, a conspicuous TSC signal was observed. Examples of the TSC signal are shown in Fig. 1(b). After measurement I was finished, the substrate was then cooled. An attempt to measure the dependence of the current on temperature was then performed, however, the TSC signal no longer appeared, as shown in Fig. 1(c) (measurement II). The TSC signal in measurement II could not be observed, even if the film was irradiated by light at a low temperature under an applied bias voltage. Therefore, the TSC is characterized by the fact that it can be observed only once. The TSC spectrum was defined by subtracting the value of current in measurement II from that in measurement I.

In this work, tetracene films were formed at $T_f=213$, 203, 193, 173, and 153 K. When the T_f had values of 193, 173, and 153 K, the TSC was observed, however, it was not observed when T_f was 213 K. The absence of the TSC was not due to the substrate or the electrodes used at 213 K. Further, when T_f was 203 K, the TSC was observed in a film of thickness less than 2×10^3 Å but could not be observed in thickness greater than that. Thus, the critical temperature for the appearance of the TSC is thought to be near 203 K.

Next, experiments were performed to confirm the appearance of the TSC with the procedure as follows.

Experiment 1. After measurement II of the film was completed, the film was exposed to the ambient air for several minutes at room temperature. Then a second tetracene film was deposited on the film at the same T_f. Furthermore, a third film was deposited in the same manner after five days. The films formed in such a manner also exhibited the TSC as shown in Fig. 2; the shape of the TSC was essentially unchanged.

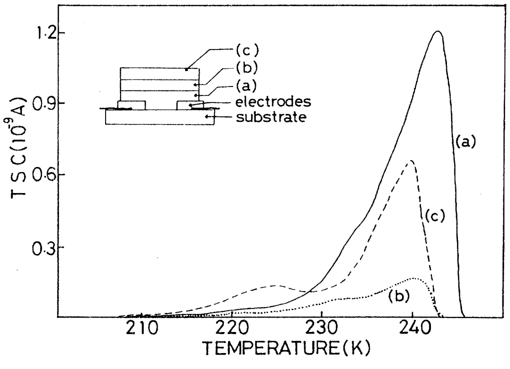

FIG. 2. Results of experiment 1 for tetracene films. The thickness and the T_f of the films (a), (b), and (c) are 13×10^2 Å and 173 K, respectively. The deposition rate and the heating rate are 10 Å/s and 4.6×10^{-2} K/s for (a), 14 Å/s and 4.8×10^{-2} K/s for (b), and 13 Å/s and 4.4×10^{-2} K/s for (c), respectively.

Experiment 2. After a film of tetracene was deposited at 173 K, the temperature of the film was raised at a constant rate through short-circuiting of the electrodes. When the temperature reached 210 K, a bias voltage of 850 V was applied while the dependence of the current on the temperature was being measured. The TSC was also observed in this case.

Experiment 3. After a film of tetracene was deposited at 173 K, its surface was contaminated by maintaining it for one hour at 173 K in a 1×10^{-1} Torr vacuum. The contaminated film also displayed the TSC.

The results of experiments 1 and 3 imply that the TSC is due to the bulk of the film. The results also confirm that the TSC is not due to the surface of the film, the boundaries between the film and quartz, or between the film and Au.

B. Pentacene

The TSC was also measured in pentacene films to compare with those of the tetracene films. The experimental procedure and conditions are same as in the case of tetracene. Figure 3 is the same as Fig. 1 except for a pentacene film. The TSC was observed under the condition of $T_f\leq190$ K, but it was not observed when $T_f=200$ K. The critical temperature for the appearance of the TSC seems to be slightly lower in the pentacene than in tetracene. While most of the peak temperature of the TSC fell between 220 and 240 K for tetracene, it was between 200 and 230 K for the pentacene films. The results from experiment 1 with tetracene films were confirmed by the experiments using pentacene films. However, the TSC of the second film was 2 orders of magnitude smaller than that of the first film. This probably results from the degree of epitaxy in the pentacene evaporation films being greater than that in tetracene.

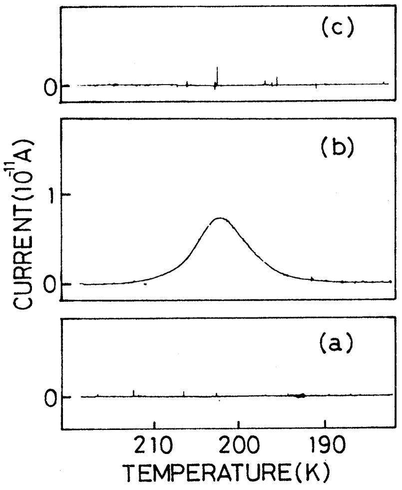

FIG. 3. An example of the TSC curve occurring in a pentacene film. Conditions of the film formation are as follows: thickness, 14×10^2 Å; deposition rate, 7 Å/s; T_f, 180 K. (a), (b), and (c) are current measured as a function of temperature for the substrate, the film in measurement I, and that in measurement II, respectively.

III. DISCUSSION

The TSC is essentially different from the so-called thermally stimulated depolarization current (TSDC).[9] In measuring the TSDC the traps are first filled by the application of an electric field across the specimen, which is provided with one blocking and one Ohmic contact. However, in the present work the electrodes are not blocking, the circuit being shorted during the formation of the film.

Since the temperature of the evaporation source was about 500 K, which corresponds to 0.04 eV for thermal energy, the kinetic energy of a molecule impinging on the surface of the film is much less than the band-gap energy of 3.4 eV for tetracene and 2.4 eV for pentacene.[10] The kinetic energy is also much less than the lowest excitation energy of 2.4 eV for tetracene and 1.8 eV for pentacene crystals. Thus it is improbable that the collision of the impinging molecule with the film surface produces free carriers in the film, owing to the band-to-band ionizing transition or autoionizing transition of an excited molecule. If the carriers are generated by some process and captured by the traps during film formation at low temperatures, the contribution to TSC curve by the carriers liberated when the temperature T is raised under an applied field can be expressed by the conventional TSC curve $I_1(T)$:[11,12]

$$I_1(T)=I_0\exp\left[-\frac{E}{kT}-\frac{f}{B}\int_{T_f}^{T}\exp\left[-\frac{E}{kT}\right]dT\right] . \qquad (1)$$

The notation is as follows: k is the Boltzmann constant, f is the frequency factor for escape from the traps, B is the heating rate, and I_0 is a constant. It is assumed that the film contains a single set of electron or hole traps, located at an energy E below the conduction or above the valence bands. However, the agreement between Eq. (1) and the experimental TSC curve is not good, as shown by the dotted line in Fig. 4, where the experimental data appear as if a single peak was selected. These results indicate that the responsible mechanism of excitation of the TSC does not exist in the film formation. This seems to be also supported by the existence of a critical temperature for the appearance of the TSC. Therefore, it can be concluded that the cause of the TSC occurs in the annealing of fresh films deposited at low temperatures.

Sakurai[13] exhibited that the TSC curves $I(T)$ caused by trapped charge-transfer (CT) excitons were expressed by

$$I(T)=\frac{I_0\exp\left[-\dfrac{E+U}{kT}-\dfrac{F}{B}\displaystyle\int_{T_f}^{T}\exp\left[-\dfrac{E+U}{kT}\right]dT\right]}{1+M\exp\left[-\dfrac{F}{B}\displaystyle\int_{T_f}^{T}\exp\left[-\dfrac{E+U}{kT}\right]dT\right]} . \qquad (2)$$

Here, the Coulombic binding energy between the electron and the hole is U. $M=\gamma\tau N_0$ and $F=fN_c/N_{\mathrm{CT}}$. N_0 is the density of trapped CT excitons while N_c and N_{CT} are the effective state densities of conduction and CT exciton states, respectively. γ is a recombination rate constant between the CT exciton and the free hole and τ is the lifetime of the free holes. The trapped CT exciton, illustrated in Fig. 5, can be written as consisting of a trapped hole with a free electron as a nearest neighbor.[14] In Eq. (2), the TSC is assumed to be the hole current. The free hole is generated by a two-step process consisting of the thermal dissociation of the trapped CT exciton into a trapped hole and of subsequent thermal release of the trapped hole into a free hole. The recombination between the free hole and trapped CT exciton also generates the trapped hole. The derivation of Eq. (2) is detailed in Ref. 13. The results of spectral fitting based on Eq. (2) are shown in Fig. 4. As illustrated, the experimental curves of the TSC agree rather well with the curve derived from the model of the trapped CT exciton. From this agreement, it is concluded that the TSC is most likely caused by the trapped charge-transfer excitons.

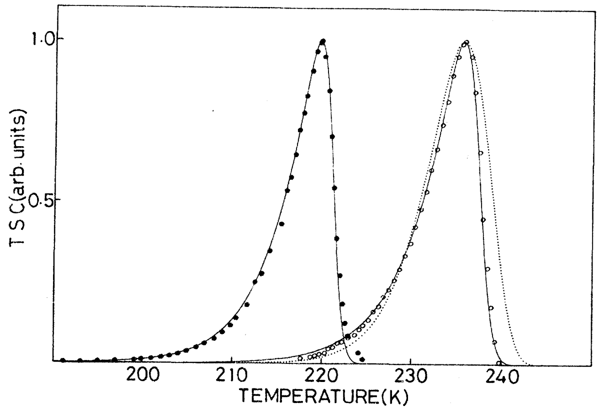

FIG. 4. Comparison of the theoretical TSC curves with the experimental data in a tetracene film (○) and a pentacene film (●). The dotted line is computed by Eq. (1) with $E=1.4$ eV. The solid lines are computed by Eq. (2) with $E+U=0.96$ eV and $F=1.7\times10^{19}$ s^{-1} for tetracene and $E+U=0.90$ eV and $F=2.4\times10^{19}$ s^{-1} for pentacene.

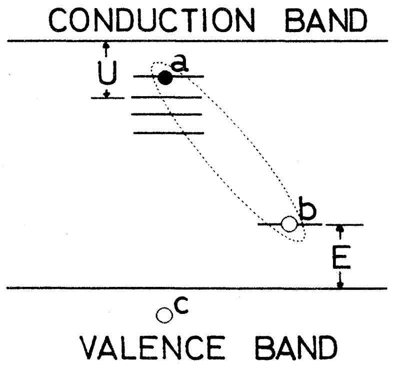

FIG. 5. Diagram of the energy-level scheme illustrating the mechanism of the TSC caused by the trapped charge-transfer exciton. a and b represent the trapped charge-transfer exciton; c is a free hole. Recombination between a and c generates a trapped hole.

The spectral fitting between Eq. (2) and the experimental curve gives a value of $E+U$. It should be noted that a trapped hole corresponds to the trapped CT exciton with $U=0$. This condition of $U=0$ implies $N_c=N_{\mathrm{CT}}$ and $\gamma=0$. Equation (1) is subsequently obtained by substituting these values into Eq. (2). Hence, if components can be found which are suitable to Eq. (1) and Eq. (2) in a TSC curve, one can distinguish between Coulombic binding energy U and conventional trap release energy E in the observation of the TSC signal. Unfortunately, the former component could not be found in the TSC without optical excitation during the annealing, but it should be present in the TSC curve with optical excitation. In fact, it has been reported that the two components coexist in the TSC spectrum, when the tetracene films depositied at room temperature are excited by 365-nm light at low temperatures. According to Sakurai,[13] the structure of the trapped CT exciton is that U is equal to 0.69, 0.58, 0.49, and 0.38 eV, with the hole being trapped at $E=0.58$ eV. The value of U is equal to E_g-E_{CT}, where E_g and E_{CT} are the band-gap and CT state energies, respectively. Energies of free CT excitons $E_{\mathrm{CT}}=2.71$, 2.78, 2.90. and 3.06 eV have been obtained from tetracene polycrystalline films by Sebastian *et al.*[10] using electroabsorption spectroscopy. Setting $E_g=3.4$ eV, one can obtain values of 0.69, 0.62, 0.50, and 0.34 eV for U of the free CT excitons. The agreement suggests that the Coulombic binding energy of the electron-hole pair is the same between the trapped CT excitons and the free CT excitons in tetracene polycrystalline films. Additional evidence for this suggestion was provided by the result of Arnold *et al.*,[14] who found that the dissociation energy of the trapped CT states was about 0.35 eV. Although an example of the difference between E and U for the tetracene film deposited at low temperatures is shown in Fig. 6, the experimental data are not sufficient to also confirm the suggestion that this occurs in low-temperature evaporation films, namely, amorphous films. However, the fact that the TSC appeared at appreciably lower temperatures in pentacene than in tetracene films may suggest that the values of U for pentacene are smaller than those of tetracene, since the values of the trap depth E caused by structural faults are thought to change slightly between tetracene and pentacene. In fact, according to Sebastian *et al.*,[10] the values of U for the free CT exciton in pentacene polycrystalline films are 0.30, 0.15, and 0.08 eV, which are much smaller than those of tetracene.

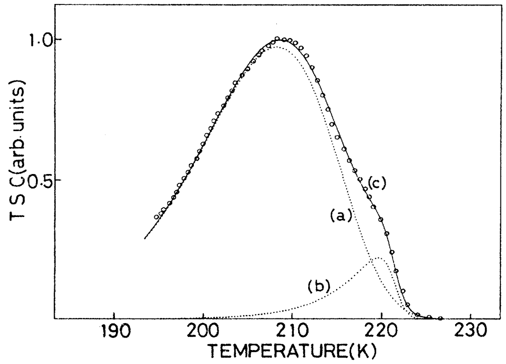

FIG. 6. An example of the difference between E and U by spectral fitting. Solid circles are the experimental TSC data of the film subjected to an optical excitation of 365-nm light at 195 K. Conditions of the film formation are as follows: thickness, 14×10^2 Å; deposition rate, 2 Å/s; T_f, 200 K. Curve (a) is computed by Eq. (1) with $E=0.48$ eV, and curve (b) by Eq. (2) with $E+U=0.83$ eV and $F=3.0\times10^{17}$ s^{-1}. Curve (c) represents the superposition of (a) and (b). The agreement between curve (c) and experimental data shows $U=0.35$ eV.

There are several pieces of evidence that indicate that crystal lattice sites where interaction between neighboring molecules becomes significantly greater than van der Walls energy exist in an aromatic hydrocarbon film deposited on a cooled substrate. Arden *et al.*[15] found that the fluorescence of the deposition films is due to emission from an excimer state. Further, Seki and Itoh[5] reported that an amount of stable dimers exists in an intermediate stage in the annealing of a thin anthracene film deposited on fused quartz, cooled by liquid He. It appears from these results that the trapped CT excitons that are responsible for the TSC are connected with such sites in the films. Further, Eiermann *et al.*[8] showed that the crystal lattices of tetracene and pentacene films deposited at $T_f<200$ K (low-temperature phase) are stressed compared with the films at $T_f>200$ K (high-temperature phase). The temperature coincides with the critical temperature for the appearance of the TSC. It seems noteworthy to focus attention on this coincidence. Eiermann *et al.* also found the dramatic change in the diffraction intensities over the same temperature interval. This suggests the existence of some reorganization within the lattice for this temperature interval. From these results it can be conceived that when tetracene and pentacene films which are deposited at $T_f<200$ K are annealed, the structure of the films transfers from the low-temperature phase to the high-temperature phase in the neighborhood of 200 K. The molecules at the sites previously mentioned are ionized by the release of strain energy during the phase transformation. The strain energy was estimated to be 0.09 eV per unit cell for tetracene and 0.05 eV for pentacene, using the data of Eiermann *et al.*[8] and the elastic stiffness constants of anthracene crystal,[16] since the constants for tetracene and pentacene crystals were unfortunately not available. With the results of Sebastian *et al.*[10] taken as the values of $E_{\mathrm{CT}}=E_g-U$, the estimate shows that one CT exciton per 30 cells (20 cells) can be formed in tetracene (pentacene) films, assuming the energy conversion efficiency is 100%. Although the efficiency is not actually 100% the production of the CT state due to phase transformation does not require the same energy as E_{CT} measured by optical absorption in a stable crystal. This is a result of the phase transformation occurring with lattice displacement and U dependence on r^{-1}, where r is the CT distance. A thermally dissociating CT pair is not in an identical state to a primary excited state.[17] That is, the next physical picture can be described. There may be some sites within the film where molecular distance becomes less than the equilibrium lattice constant or the overlap of the π orbit-

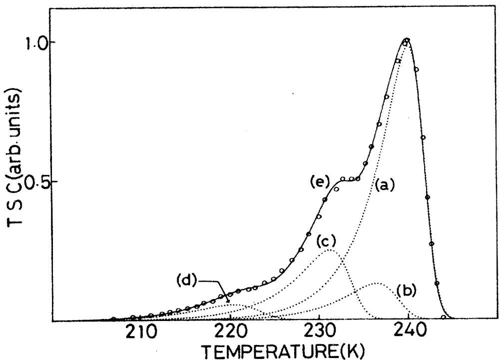

FIG. 7. Spectral fitting of the TSC shown in Fig. 1. Solid circles are the experimental data. Curves (a)–(d) are computed by using Eq. (2) with $E+U=1.17$ eV, $F=1.5\times10^{23}$ s^{-1}; 1.1 eV, 7.6×10^{21} s^{-1}; 0.98 eV, 6.8×10^{19} s^{-1}; and 0.82 eV, 1.1×10^{17} s^{-1}, respectively. Curve (e) represents the superposition of curves (a)–(d).

als becomes greater than that in the equilibrium orientation on the occurrence of the phase transformation. At this site, a charged carrier is able to jump with smaller energy than the values of E_{CT} mentioned above, and afterwards the lattice relaxation energy can be delivered to the CT pairs. Therefore, the CT states are most likely caused by the phase transformation in annealing. This view can easily explain the dependence of the TSC on the thickness of the tetracene films deposited at 203 K. The results of experiments 1, 2, and 3 are also consistent with this view.

The literature also offers evidence to support this view. That is, the phenomenon of electron emission resulting from the energy transfer of mechanical energy to electronic energy is known as the Kramer effect,[18] and is called exoemission. The exoemission has been observed during ongoing changes in the state of aggregation.[19] Furthermore, the idea that internal ionization is caused by a mechanical stress was proposed by Zakrevskii and Pakhotin,[20] who reported the emission of electrons from a stretched polymer into a vacuum. Interestingly, there are phenomena in which exoemission maxima are shifted against the temperature of phase change.[21] Since Arnold *et al.*[14] showed that an electron was emitted as a result of an Auger-like transition with a trapped CT exciton, these phenomena can also probably be explained by the production of trapped CT exciton due to phase transformation.

Although it was pointed out that CT states can be formed at a molecular-crystal–metal interface as a result of dark field injection of charge carriers,[22] the results of experiments 1 and 2 indicate that this is inadequate to be considered an origin of the TSC.

Almost all the TSC spectra as shown in Fig. 1 can probably be interpreted as an overlap of TSC's caused by several trapped CT states. For example, the spectrum of Fig. 1 agrees with that shown in Fig. 7 if E is taken to be 0.48 eV, according to the result of Fig. 6. The criterion for the overlapping procedure will be discussed elsewhere.

IV. CONCLUSIONS

The TSC in the absence of optical excitation was observed in tetracene and pentacene films deposited under the conditions $T_f \leq 203$ K and $T_f \leq 190$ K, respectively. This is most likely caused by the trapped charge-transfer excitons. They are probably formed in the intermediate stage of the annealing temperature change where the strain energy is released from the stressed crystal lattices in the films. Thus, the TSC was only observed once in fresh films deposited at low temperatures.

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