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VACUUM DEPOSITION OF A QUINOLINIUM(TCNQ)$_2$ THIN FILM

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A thin film of a highly conducting organic semiconductor was obtained by direct evaporation of quinolinium(TCNQ)$_2$ ion-radical salt. The temperature of the evaporation source was controlled so as to prevent the salt from decomposing and dissociating. Optical and electrical properties were investigated on the vacuum-deposited thin films.

A major difficulty encountered in the experimental studies of highly conducting organic semiconductors based on 7,7,8,8-tetracyanoquinodimethan (TCNQ) ion-radical salts lies in the fact that large single crystals are available only for limited cases. Since most of the TCNQ salts on heating decompose over a wide temperature range,$^{1)}$ preparation of thin films by direct evaporation of these salts has never been successful.$^{2)}$ Thin films of certain salts can be prepared by simultaneously or successively evaporating the components from separate sources. This letter reports some evidences for the direct evaporation of quinolinium(TCNQ)$_2$ (Q(TCNQ)$_2$), along with brief references to optical and electrical properties of the evaporated thin films.

As Siemons, Bierstedt and Kepler stated,$^{3)}$ complex TCNQ salts, $M^+TCNQ^{\cdot}TCNQ^\circ$, on heating dissociate into neutral TCNQ and simple salts of the type, $M^+TCNQ^{\cdot}$, and most of the simple salts decompose before melting. When a pressed pellet of Q(TCNQ)$_2$ was gradually heated in vacuum, a yellow component (TCNQ$^\circ$) volatilized at 74°C, blue powders being left on the pellet; then a brown to black material, consisting mainly of Q(TCNQ)$_2$, sublimed above 110°C. The initial preferential evaporation of a component is similar to a complication in the evaporation of alloys and compound semiconductors. We found, however, that quick elevation of the source temperature was effective for preventing the salt from fractionally distillating. The method is in principle analogous to flash evaporation$^{4)}$ employed in preparing thin films of those easy-dissociating inorganic materials, though grain-by-grain evaporation was not used in this case. A small block of pressed powders of Q(TCNQ)$_2$ was placed directly in a tungsten basket, and the evaporation source was heated at the rise rate of about 10°C/sec to a temperature higher than 120°C. Homogeneous films were deposited on substrates about 5 cm apart from the source. Decomposed products which were characterized by optical absorption (in acetonitrile solution) at 470 mμ in wavelength was not detected as long as the source temperature was maintained between 120 and 200°C.

The molar ratio of neutral to ion-radical TCNQ can be estimated from the ratio of optical density at 395 mμ (TCNQ$^{\circ}$ + TCNQ$^{\overline{\cdot}}$) to that at 842 mμ (TCNQ$^{\overline{\cdot}}$), where the ratio is about 2.0 for a stoichiometric complex salt (TCNQ$^{\circ}$/TCNQ$^{\overline{\cdot}}$=1).$^{1)}$ The TCNQ$^{\circ}$/TCNQ$^{\overline{\cdot}}$ ratio depended on the film thickness and the evaporation rate: for a 900 Å thick film evaporated at the rate of 50 Å/sec the ratio of optical densities was 2.60 which means that the molar ratio is 1.5, and for a film 2800 Å thick (90 Å/sec) the ratio of optical densities was 2.31 and the molar ratio 1.2. When the initial fraction corresponding to a thickness of about 2000 Å was discarded using a shutter, the evaporated material was regarded as a stoichiometric complex salt (the ratio of optical densities was smaller than 2.02 as is shown in Fig. 2.) Fig. 1 shows the infrared spectra of evaporated films of TCNQ and Q(TCNQ)$_2$. The IR spectrum of an evaporated Q(TCNQ)$_2$ film exhibited all the absorption bands characteristic of a complex salt which may arise from resonance between TCNQ$^{\overline{\cdot}}$ and TCNQ$^{\circ}$: a considerably broadened -C≡N band at 2210-2000 cm^{-1} with sharp lines at 2206 and 2199 cm^{-1} and strong and broad bands at 1550, 1520, 1300, 1100, 800 and 680 cm^{-1}. Absorptions ascribable to the non-interacting TCNQ$^{\circ}$ were thought to be absent from the spectrum of Q(TCNQ)$_2$. The spectrum was also characterized by well resolved cation absorptions below 1700 cm^{-1}.

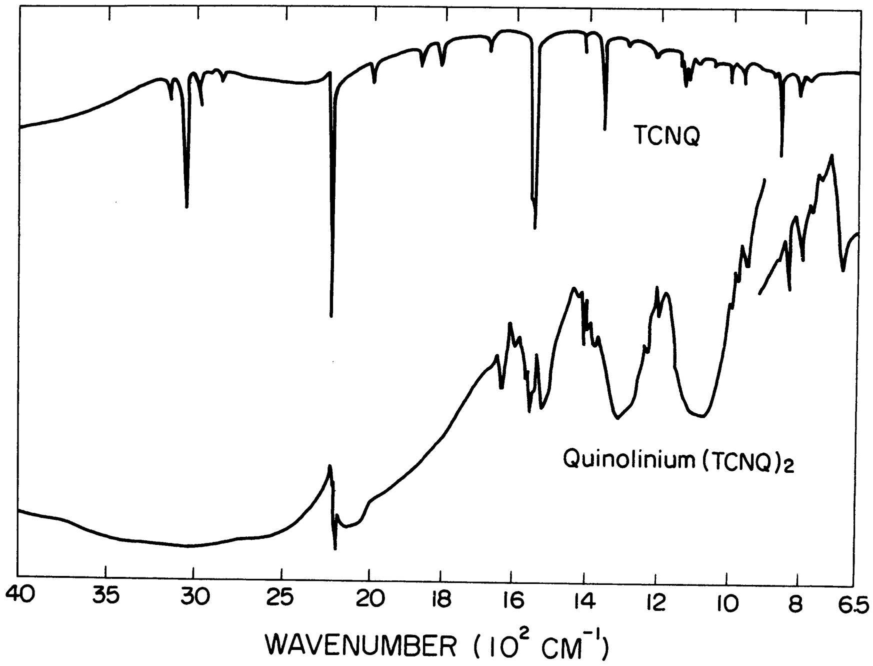

Fig. 1. Infrared absorption spectra of vacuum-deposited films of TCNQ and quinolinium(TCNQ)$_2$

Fig. 2 shows the electronic absorption spectra of Q(TCNQ)$_2$ evaporated on both quartz and freshly cleaved sodium chloride plates. These spectra in general coincide with those of complex TCNQ ion-radical salts measured by means of diffuse reflectance.$^{5)}$ An absorption band associated

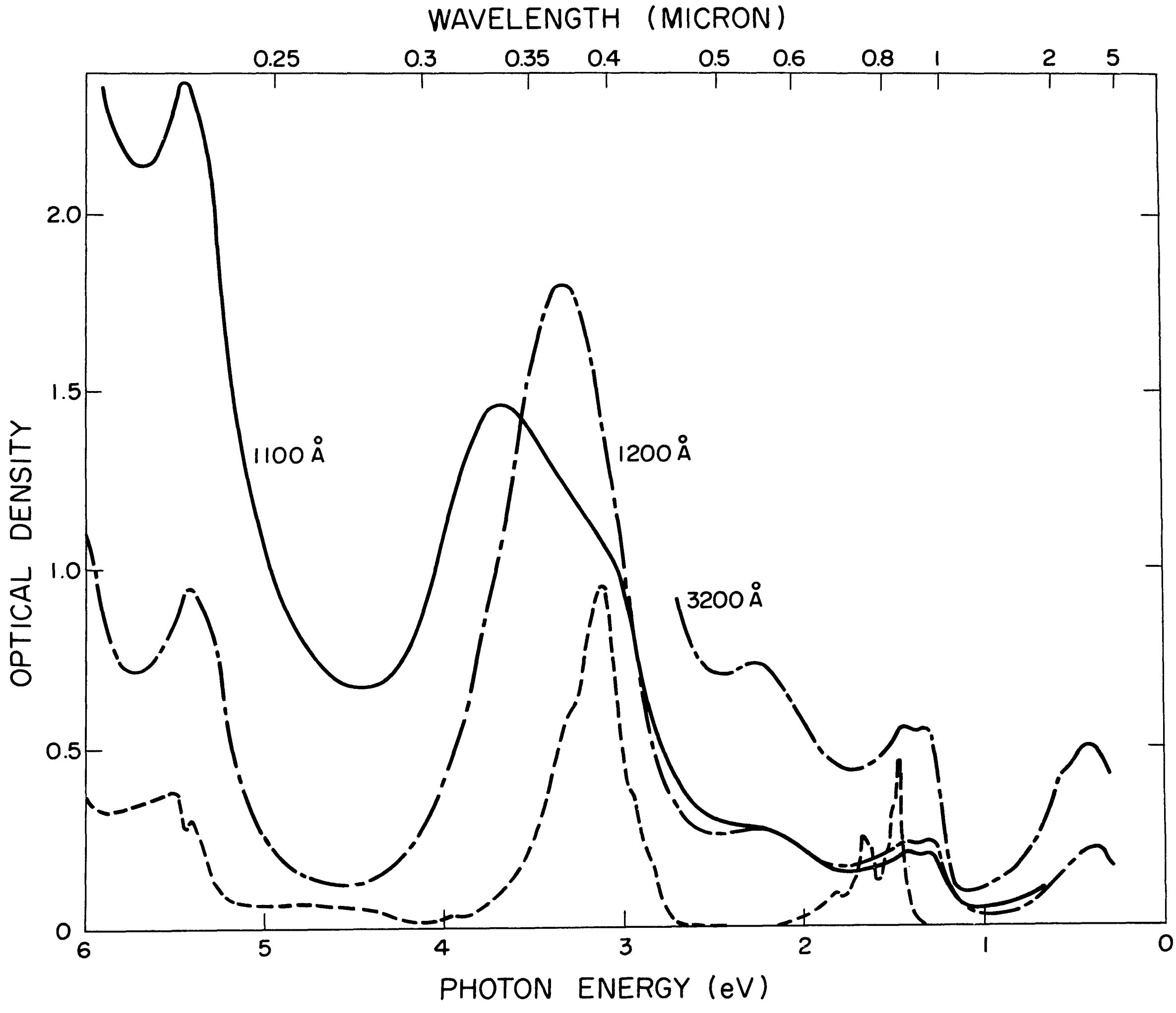

Fig. 2. Electronic absorption spectra of vacuum-deposited films of quinolinium(TCNQ)$_2$ on quartz (————) and on NaCl crystal (— — — —), and in acetonitrile solution (– – – – – –).

with charge-transfer interaction between TCNQ$^{\dot{-}}$ and TCNQ$^{\circ}$ was found at 0.37 eV, and contrary to the diffuse reflectance data, two distinct peaks were found at 1.31 eV and 1.44 eV. The band at 2.26 eV was blue-shifted to 2.55 eV in an absorption spectrum of Q(TCNQ)$_2$ dissolved in polyacrylonitrile which is known as a polymer capable of forming a complete solid solution of TCNQ salts.$^{6)}$ This fact suggests that the band is also related to a charge-transfer transition. There was a striking difference in the absorption spectra in the local excitation region, 3-6 eV, between substrates on which Q(TCNQ)$_2$ films were deposited. This difference may suggest that the homogenity and the crystallinity of the evaporated films strongly depend on the substrates used.$^{7)}$

The electrical conductivity of the films deposited on slide glasses was measured on a surface type cell with evaporated gold electrodes (spaced 0.25 mm apart). For films of thicknesses from

500 up to 6000 Å, the conductivity was 1 mho/cm, which is about a third of that of compacted powders. The activation energy for conduction varied from 0.05 eV for a film of 1600 Å thick to 0.03 eV for films thicker than 10 μ. The insulator-metal transition was not observed over the temperature range measured (200-346°K). The upper limit of conductivity measurement was set by some kinds of decomposition of the evaporated film which led to irreversible change in conductivity. Crystal analysis and dependences of conductivity and activation energy on the film thickness are in the cource of study.

Concludingly, we suggest that vacuum deposition of quinolinium$(TCNQ)_2$ is realized, and that it may be applied to various investigations on solid state properties of this material.8)

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