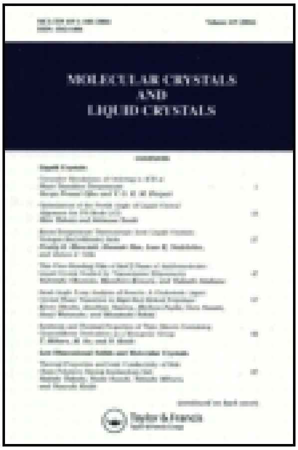

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Thin Films of Alkali-Dcnqi Radical Ion Salts

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THIN FILMS OF ALKALI-DCNQI RADICAL ION SALTS

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Abstract Thin films of conducting radical ion salts (RIS) with predefined anisotropic behaviour have been investigated with respect to their optical and electronic properties. Photoinduced differences in the film growth enable the preparation of conducting structures in these thin films.

INTRODUCTION

Low dimensional organic conductors have been attracting considerable attention. Recently, dicyanoquinonediimine (DCNQI) radical ion salts with different metallic counterions have been investigated by several groups[1,2,3,4]. With respect to future technical applications, the processing and the properties of thin films of these salts have been investigated using the recently developed method of a diffusion controlled reaction. First results of optically structured films are presented. We focus on the alkali 2,5-dimethyl-DCNQI salts and their properties in experiments dealing with optical absorption, electron spin resonance, conductivity, and photoelectron emission.

EXPERIMENTAL

Thin films of the DMe-DCNQI radical ion salts have been synthesized by subsequent vacuum deposition of the neutral organic molecules and the alkali metals onto cooled substrates[5]. Parts of the films have been irradiated at 77 K using an arc lamp (HBO 500) equipped with bandpass filters for the mercury 366 nm line, which is close to the absorption maximum of the neutral DCNQI molecules in the film. All films (exposed and unexposed) have been carefully heated to room temperature. The thickness range, which was accessible by three layer structures, comprised 40 nm to 200 nm. Figure 1 gives the sample structure.

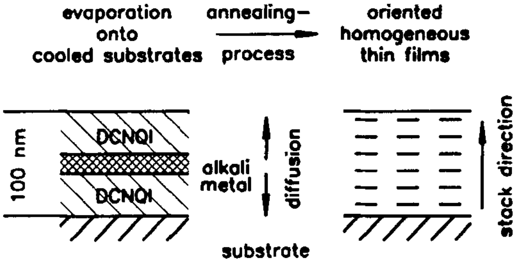

FIGURE 1
Preparation of thin RIS films and idealized arrangement of flat molecules in the annealed film.

Optical absorption spectra and conductivity measurements were performed in situ using a modified Cary 14 spectrometer and an HP 3457A multimeter. The samples were transferred to the ESR apparatus (Varian E-Line) in an inert N_2 atmosphere.

RESULTS AND DISCUSSION

Annealed conducting films without optical exposure

Optical absorption spectra have been used to monitor the course of the solid state reaction between the DCNQI and the alkali metal. At 77 K, the spectra do not change with time, i.e. the reaction is suppressed, with the exception of the directly interfacing layers. The absorption spectra of the multilayer alkali DMe-DCNQI films are given in fig. 2. During the annealing process, the intensity of the band at 350 nm, assigned to neutral DCNQI, decreases and new bands around 700 nm raise (dotted line), where the absorption of DCNQI$^-$-anions is expected.

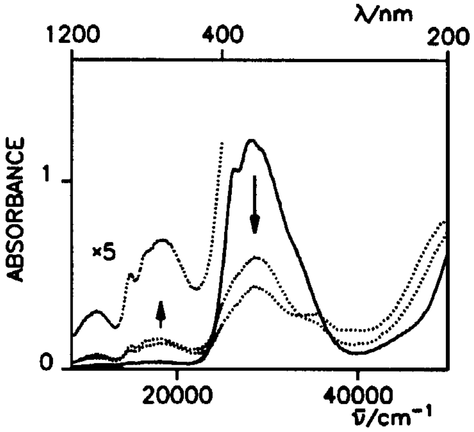

FIGURE 2
Change of absorption spectra during the annealing of an unexposed three layer structure of Cs(DMe-DCNQI)$_2$.
— evaporated multilayer film
••• annealed film (100nm) after 10h and 30h
×5 magnified

In comparison with the solution spectra, the film spectra are broadened and red-shifted. The contributions of the neutral and the anion molecules can be distinguished in analogy to the TCNQ bands by reflection spectroscopy on single crystals[4]. In the case of thin films the change of the absorption spectra in the run of the annealing process indicates the reaction in the low dimensional salts.

Anisotropy

ESR measurements on the radical ion salt thin films prove the formation of spin carriers and demonstrate the anisotropy of the films. The films show anisotropic behaviour which is well known from the DCNQI single crystals[2]. Fig. 3 gives the angular dependence of the g-factors of the alkali DMe-DCNQI radical ion salt films. The orientation dependence refers to the angle between the film plane and the static magnetic field. In comparison with single crystal work, the preferential molecular stacking direction is determined to be perpendicular to the film plane[5,6]. Assuming a Gaussian distribution of the stacking directions the distribution parameter σ is smaller than 20^0 in good films of all alkali salts thinner than 150nm. In thick films (200nm) the g-factor anisotropy is reduced, however. This decrease of the anisotropy can be qualitatively understood as the concentration gradient decreases at the diffusion front whenever it has to cover long distances. Thus the preferential orientation is not as well defined as with thinner samples. Higher thickness and still a high anisotropy seem to be in reach only by the use of an increased number of subsequent layers.

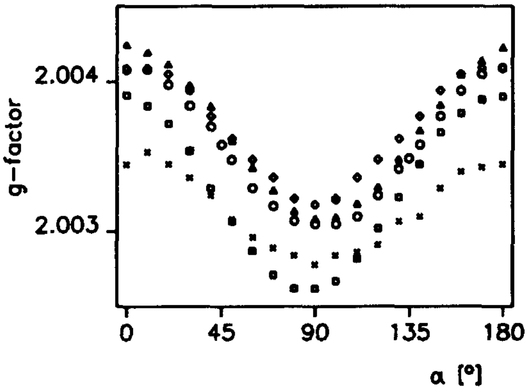

FIGURE 3

Anisotropy of the g-factor in alkali DMe-DCNQI films (100nm thick), determined by ESR.

◇ $Li(DMe\text{-}DCNQI)_2$
□ $Na(DMe\text{-}DCNQI)_2$
△ $K(DMe\text{-}DCNQI)_2$
○ $Rb(DMe\text{-}DCNQI)_2$
× $Cs(DMe\text{-}DCNQI)_2$

Conductivity

The anisotropy of the conductivity was estimated by frequency dependent NMR of single crystals. A ratio of $\sigma_{\parallel}/\sigma_{\perp} \approx 6000$ could be determined[7]. Because of the preferential orientation of the films, the conductivity data displayed in fig. 4 correspond to a high degree to the lower conducting direction and are influenced by grain boundaries and the statistical orientation of the stacks. All films show a thermally activated conductivity. The activation energy ΔE_a defined by the equation $\sigma = \sigma_0 \bullet \exp[-\Delta E_a/kT]$ is very small, $\Delta E_a = 0.07$ eV (Li, K, Rb salt films) and is higher in the case of Na and Cs salts. However, in comparison with single crystals the activation energies ΔE_a are larger in thin films. In general, the conductivity of these materials can be considered to be proportional to the product of the concentration of charge carriers and the mobility. In contrast to the Epstein formula, which yields a good description of the single crystal conductivity in the highly conducting direction, the temperature dependence of the mobility μ is not described by a power law $T^{-\alpha}$ but can be included in the activated term, so we finally observe the overall activation energy $\Delta E_a = \Delta E_c + \Delta E_{tf}$. Here ΔE_c is the activation energy in single crystals, which results from the carrier concentration and ΔE_{tf} is the activation energy of the mobility, which seems to be considerably influenced by grain boundaries and other deviations from the ideal crystalline films. Experimentally, the electronic structure of some alkali DCNQI salt films was accessed by UPS investigations[8] which confirm the semiconducting properties of these salt films. As in other low-dimensional systems, the gap between the Fermi level of a clean metallic reference and the onset of the photoemission is larger than the activation energy ΔE_a. From the comparison of Cu and Ag salts containing d-states with DCNQI systems without the interference of d-states it can be shown that the contributions of C2p and N2p molecular orbitals in the valence band are dominantly responsible for the conduction mechanism.

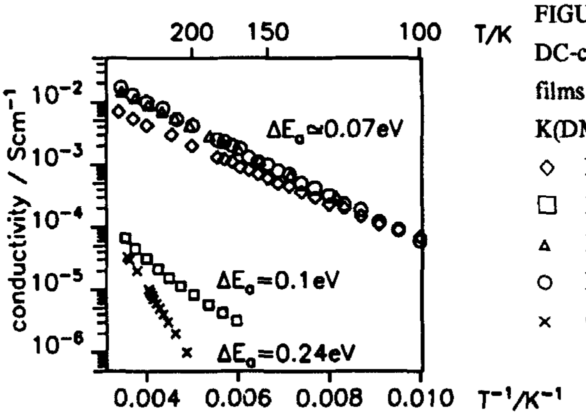

FIGURE 4
DC-conductivity of alkali DCNQI thin films. Thickness normally 100nm, $K(DMe\text{-}DCNQI)_2$: 200mn.

◇ $Li(DMe\text{-}DCNQI)_2$
□ $Na(DMe\text{-}DCNQI)_2$
▵ $K(DMe\text{-}DCNQI)_2$
○ $Rb(DMe\text{-}DCNQI)_2$
× $Cs(DMe\text{-}DCNQI)_2$

Films exposed to UV before annealing

At 77 K, the band at 350 nm, which is ascribed to the π-π^*-transition of the neutral DCNQI, can be changed by the irradiation of UV light without any corresponding production of the bands around 700 nm. Instead, an enhancement of the absorption at higher photon energies between 300 nm and 200 nm is observed. This is displayed for a film of $K(DMe\text{-}DCNQI)_2$ (thickness 100 nm) in fig. 5. During the subsequent annealing process, the features typical for DCNQI salt films, e.g. high conductivity and intense ESR signals, are only found in those regions of the films that had not been exposed to light. As the samples had been kept at 77 K, a desorption of the organic material can be excluded incontrast to photoablation[9] at elevated substrate temperatures. The formation of an energetically higher broad absorption hints at a photoinduced destruction of the DCNQI molecules. This is supported by X-ray investigations of these films yielding only a diffuse background, the lack of a $DCNQI^-$-anion like absorption in the annealed films, and the absence of electron spins. These results demonstrate that it is possible to cause light induced insulating regions in the film plane and encourage the design of further structures on the submicrometer scale.

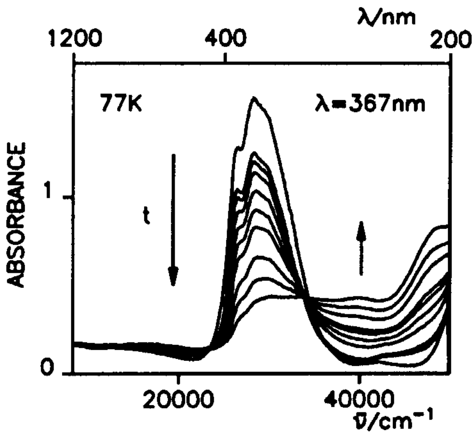

FIGURE 5
Change of absorption spectra of a $K(DMe\text{-}DCNQI)_2$ film at 77 K due to irradiation of UV light (λ=366nm). Thickness 120nm. The DCNQI band decreases, as the energetically higher absorption increases.

Total time of irradiation: t= 0, 10, 30, 60, 90, 120, 150, 250, 390, 600 minutes.

CONCLUSION

As far as the preparation of thin films is concerned, our approach takes advantage of comparatively small molecular units, which undergo a controlled reaction with the alkali atoms. The crystal structure, known from single crystal work, shows large channel-like spacings, which allow the diffusion of the comparatively small alkali ions. Thus the material required for the reaction is not only supplied by grain boundaries but can diffuse through the already formed salt layer. In our two-component systems, diffusion along the concentration gradient between the different layers of the films favours the growth of stacks which are perpendicular to the film plane. In addition, the flat molecular geometry yields a high probability to force the molecules of the first layers in a position parallel to the substrate. In the case of alkali DCNQI films, the diffusion and the reaction of the two components are monitored by UV-VIS absorption spectroscopy and the onset of the conductivity during annealing. The physical properties of the annealed films have been investigated by electron spin resonance and by photoelectron emission.

The anisotropic charge- and spin-transport of the films and the possibility to control their reaction by irradiation of light make the films interesting candidates for interconnecting elements in molecular electronics. Further aspects are seen in the extreme sensitivity of the ESR linewidth to the exposure of molecular oxygen even at low concentrations[6].

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