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# ELECTRONIC TRANSPORT IN CRYSTALLINE SILOXENE

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For the planar silicon polymer siloxene, the anisotropy of the dark conductivity is determined to be about $10^3$, with a conductivity parallel to the silicon planes of $10^{-11}$ $(\Omega\text{-cm})^{-1}$ and perpendicular to the planes of $10^{-14}$ $(\Omega\text{-cm})^{-1}$ at 250°C. An activation energy of 1.25 eV is determined, which is approximately half of the optical bandgap. A pronounced photoconductivity is found, which is several orders of magnitude larger than the dark conductivity. At low temperatures, the photoconductivity is thermally activated with an activation energy of 40 meV. The same energy is found for the Urbach-slope parameter in the subgap absorption of siloxene crystals determined with photothermal deflection spectroscopy. © 1997 Elsevier Science Ltd. All rights reserved

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## 1. INTRODUCTION

The planar structure of siloxene ($Si_6O_3H_6$), which consists of Si-planes made of 3-fold coordinated silicon atoms [1, 2] leads to a variety of interesting physical properties of this material [3]. Most notable is the direct-gap bandstructure, which results in an efficient photoluminescence around 2.4 eV [4]. The material therefore is a promising candidate for silicon-based electroluminescence. However, the electronic transport properties, doping as well as contacts have to be understood to achieve efficient electroluminescence. First measurements of the dark conductivity of polycrystalline siloxene powder have shown typical activation energies of 1.1 eV [5]. Of particular interest is whether the anisotropy in the structure of siloxene results in an anisotropic conductivity as seen in other oriented or layered materials. Examples are stretched *trans*-polyacetylene with a ratio of the photoconductivity $\sigma_{ph}$ parallel to the polymer chains to $\sigma_{ph}$ perpendicular of 50 [6] and graphite with a ratio of the dark conductivity $\sigma$ parallel to the planes to $\sigma$ perpendicular of up to $10^4$ depending on the quality of the crystal [7]. In this Communication, we present results of the dark conductivity in crystalline siloxene. In addition, the crystalline samples allow us to investigate the photoconductivity both dependent on temperature and on excitation energy.

## 2. SAMPLE PREPARATION AND EXPERIMENTAL SETUP

Siloxene crystals were produced according to the recipe by Wöhler by transformation of $CaSi_2$ crystals with HCl (37%) at 0°C [8]. Commercially available $CaSi_2$ crystals of typically 3 mm edge length were used. Due to the topochemical reaction and the weakness of the interlayer bonding, the crystal cleaved during transformation, resulting in siloxene crystals of typically 10–100 $\mu$m thickness. The crystallinity of the siloxene obtained was checked with the help of Laue diffractograms which show a 6- resp. 3-fold symmetry axis [9]. Azimuthal streaks in the diffractogram, which indicate disorder with respect to rotation around the *c*-axis perpendicular to the planes were limited to below 5° showing a high degree of stacking order throughout the sample thickness. The pronounced radial streaks observed, on the other hand, point to asterism due to corrugated siloxene planes which are also visible when looking at the edge of the samples with the help of scanning electron microscopy. The siloxene crystals exhibit the same photoluminescence peak at 2.4 eV as the corresponding polycrystalline samples. To prevent significant chlorine contamination, which might influence the conductivity measurements, the samples were washed repeatedly in water. Using energy dispersive X-ray spectroscopy (EDX), the chlorine concentration in the siloxene samples used for this study was determined to be below the detection limit of 1%.

Two different contact geometries were used for the conductivity measurements: For transport parallel to the planes, crystals were mounted on sapphire substrates and silver paste contacts were applied (3 mm distance). For transport perpendicular to the planes, crystals were sandwiched between two indium-tin oxide (ITO) coated glass substrates. Dark conductivity measurements using silver paste coated glass plates in sandwich geometry showed that the change in metal does not influence the conductivity measurements significantly. The samples were then mounted in an optical cryostat which could be temperature controlled from 77 to 700 K. Spectrally resolved photoconductivity measurements were performed using a tungsten-halogen lamp and a 1/8 m monochromator.

## 3. RESULTS

Figure 1 shows a compilation of the dark conductivity properties of siloxene crystals in an Arrhenius plot. Previous measurements have shown that the conductivity is seriously influenced by water which is either adsorbed or still present from the chemical transformation. Values characteristic for siloxene have therefore only been obtained above 200°C. On the other hand, siloxene undergoes a structural change to an amorphous state accompanied by a change in bandstructure at temperatures above 300°C, which limits the temperature range available for the determination of the activation energy. However, below this temperature, the changes are small such as a shift in the bandgap of less than 0.15 eV [10].

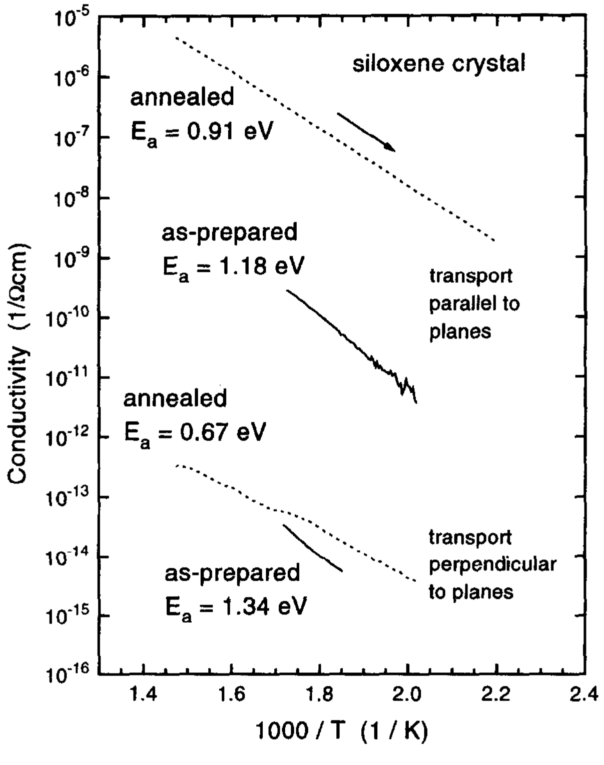

Fig. 1. Arrhenius plot of the dark conductivity of siloxene crystals for transport parallel and perpendicular to the planes: As-prepared Wöhler siloxene (straight lines) and after anneal at 680 K for 7 h (dotted lines).

Activation energies $E_a$ of 1.2–1.3 eV are observed in as prepared siloxene crystals as expected for an undoped semiconductor with a bandgap of about 2.5 eV. The absolute values for the conductivity in the two crystal orientations, however, differ significantly: At 250°C, the conductivity parallel to the planes typically is $\sigma_{\parallel} = 10^{-11}$ $(\Omega\text{-cm})^{-1}$, while the conductivity perpendicular is $\sigma_{\perp} = 10^{-14}$ $(\Omega\text{-cm})^{-1}$, an anisotropy of $10^3$. In oriented polysilane films, a similar anisotropy of two orders of magnitude has been observed recently [11]. In polycrystalline siloxene $\sigma = 10^{-13}$ $(\Omega\text{-cm})^{-1}$ was observed at 250°C, between the values for $\sigma_{\parallel}$ and $\sigma_{\perp}$ as expected for a disordered powder [5]. Extrapolating the data observed for $\sigma_{\parallel}$ we can estimate $\sigma_{\parallel}(300\text{ K}) = 10^{-19}$ $(\Omega\text{-cm})^{-1}$. Using the minimum metallic conductivity $\sigma_{\min}$

$$\sigma = \sigma_{\min} \exp[-(-E_C - E_F)/kT], \tag{1}$$

we can finally estimate the inelastic electronic scattering length $L$ from [12]

$$\sigma_{\min} = 0.03e^2/\hbar L. \tag{2}$$

With the observed activation energy of typically 1.25 eV, $L$ is approximately 100–150 Å, which is considerably larger than the corresponding values for amorphous semiconductors.

Anneal above 300°C leads to an amorphisation and a decrease of the band gap to about 1.9 eV as seen in photoluminescence [10]. A corresponding decrease in the activation energy of the dark conductivity upon anneal of the siloxene crystals in vacuum for several hours is observed, together with an increase in the absolute value of the conductivity. The origin of the increased anisotropy is not understood. Several possible explanations exist. Differences in the thermal behaviour of the contacts such as indiffusion of silver can be excluded from measurements of $\sigma_{\perp}$ using silver paste coated glass plates as mentioned above. It appears more likely that the behaviour is linked to the gradual vacuum anneal of the siloxene samples in the present work in contrast to the abrupt anneal at ambient atmosphere performed previously. The structural properties of the siloxene samples thus obtained should be subject to further investigation. However, since any anneal is likely to lead to a loss of the direct bandgap, the properties of the annealed crystalline siloxene are of less interest and we will therefore continue our discussion of conductivity properties of unannealed samples.

The photoconductivity observed in polycrystalline siloxene was in the best case of the order of the dark conductivity [5]. In crystalline siloxene, however, a much more pronounced photoconductivity was observed, allowing both measurements of its spectral resolution as well as measurements to low temperatures. Dark and photoconductivity measured parallel to the planes are shown in an Arrhenius plot in Fig. 2, together with the temperature dependence of the photoluminescence intensity taken from [14]. Under illumination with 1.5 W cm$^{-2}$ of the 514 nm line of an Art$^+$-laser, an increase of the conductivity by $10^3$ is observed at 400 K, irrespective of the transport direction. As a function of the light intensity $I$, the photoconductivity $\sigma_{ph}$ increased sublinearly with $\sigma_{ph} \propto I^{0.65}$. This shows that bimolecular recombination of light-generated electrons and holes is the dominant carrier loss mechanism as opposed to recombination via defects.

Photoluminescence excitation experiments have shown that the luminescence of siloxene can be excited resonantly just below the bandgap, typical for an excitonic system. Such a photogenerated exciton can either recombine under emission of light, or it can be broken up thermally, leading to photoconductivity. One should therefore expect that as the photoluminescence decreases with increasing temperature, the photoconductivity increases. Qualitatively, this is indeed the case as seen in Fig. 2. However, at low temperatures, the photoconductivity $\sigma_{ph,\parallel}$ shows a pronounced thermally activated behaviour with $E_a = 40$ meV, while the photoluminescence intensity is nearly constant. This fact can be understood by assuming that the bandgap in the siloxene crystal is not spatially constant but undulates slightly with a typical change of about 40 meV. Carriers at the bandedge require thermal energy to pass over these undulations, resulting in an effective mobility which is thermally activated.

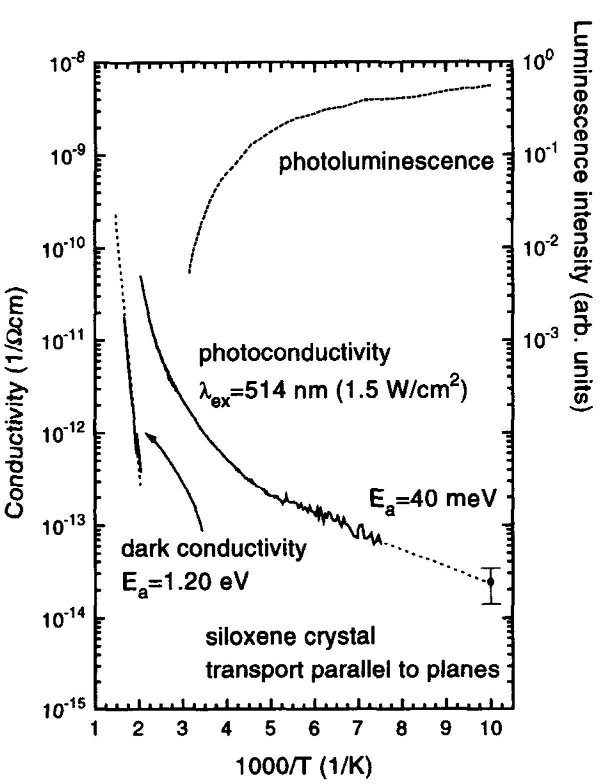

Fig. 2. Comparison of the dark and photoconductivity parallel to the planes of as-prepared Wöhler siloxene crystals and of the photoluminescence intensity.

Indeed, the distribution of the size of the bandgap is seen as an Urbach-edge slope in optical absorption measurements on siloxene crystals. Figure 3 shows the absorption coefficient of crystalline siloxene as determined with photothermal deflection spectroscopy (PDS) [15]. The data are normalized and no absolute value of the absorption coefficient is given, which would require to know the exact optical thickness of the crystal measured. However, due to internal scattering the optical thickness seems to be much larger than the crystal thickness. The same scattering also makes transmission experiments above bandgap, which could nicely show the two-dimensionality of the band structure, very difficult. The slope of the absorption tail is about 40 to 45 meV, in excellent agreement with the activation energy for $\sigma_{ph,\parallel}$ measured below 200 K. The low subgap absorption corroborates the low defect density already deduced from the intensity dependence of the photoconductivity.

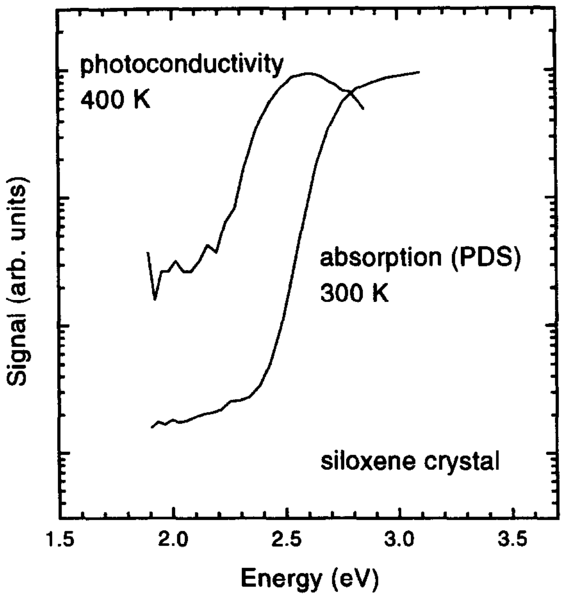

Fig. 3. Normalized absorption and photoconductivity spectrq of Siloxene crystals. The photoconductivity is measured parallel to the siloxene planes.

Finally, the influence of surface recombination is studied with the help of spectrally resolved photoconductivity. The data, also normalized, are included in Fig. 3. A slightly larger Urbach slope of 50 meV is found. For strongly absorbed light above 2.6 eV, the increase in recombination at the more defective surface can be seen as a decrease in the photoconductivity.

## 4. CONCLUSION

Two relevant aspects of electronic transport in siloxene have been studied in this communication: The anisotropy of the conductivity, which is to be expected from the layered structure of the material was determined to be typically $10^3$ in both dark conductivity and photoconductivity. A large photoconductivity, a prerequisite to electroluminescence, has been observed in siloxene crystals. However, to achieve efficient electroluminescence, *p*- and *n*-type doping or injecting contacts still have to be developed.

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