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Transport Properties of Siloxene

By

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The transport properties of siloxene (as-grown and annealed) are investigated. The dark conductivity is thermally activated with an activation energy of about 1 eV for as-prepared siloxene, in accordance with the insulating nature of this material and its energy gap of about 2.6 eV. The conductivity is very sensitive to the presence of ambient gases. The spectral and temperature dependence of photoconductivity is also discussed.

1. Introduction

Siloxene ($Si_6O_3H_6$) is a silicon compound which shows a strong visible photoluminescence comparable to that of porous silicon, and is thus an alternative material for Si-based luminescent devices. Different siloxene modifications can be obtained via the reaction of HCl with $CaSi_2$ depending on the reaction conditions applied [1 to 5]. However, so far nothing is known about the transport properties of siloxene in its different states (as-prepared, annealed, contaminated, etc.). Here we present first results concerning dark and photoconductivity of siloxene using different sample structures.

2. Experimental Details

The samples have been prepared in two different ways. For type-I samples, Wöhler siloxene powder produced by the reaction of a 37% HCl solution in water with $CaSi_2$ was dissolved in a suitable solvent (e.g. ethanol) and then applied to a conducting substrate (indium–tin–oxide or crystalline Si). After evaporation of the solvent, layers with typical thicknesses between 50 and 200 μm were obtained. Type-II samples were produced by evaporating Ca onto hot crystalline Si substrates ($T \approx 730\ °C$), thereby producing quasi-epitaxial layers of $CaSi_2$. These layers were subsequently transformed into siloxene via exposure to a 37% HCl solution in water. Further details of the preparation procedure can be found in [6]. The conductivity measurements were performed in vacuum ($< 10^{-3}$ Pa) or in certain gas atmospheres (H_2O, nitrogen, oxygen, or ethanol). The sample was heated to a temperature between 400 and 650 K for some time to outgas and then cooled down to room temperature slowly while measuring the dc conductivity using a Keithley 617 electrometer.
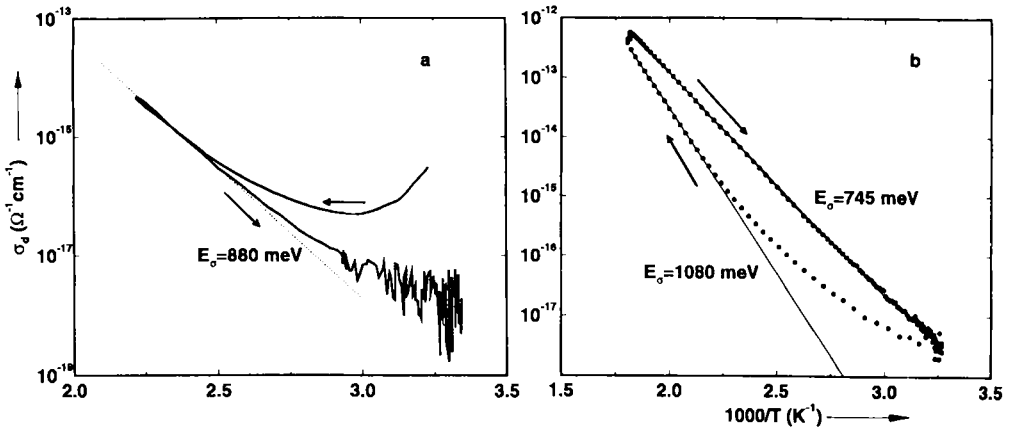
Fig. 1. Arrhenius plot of the conductivity of siloxene powder in vacuum. After evaporation of adsorbed contaminants the conductivity shows a thermally activated behavior. a) A typical measurement taken with a sample which has been exposed to air. b) Increase of conductivity after annealing the sample for 10 min at 280 °C

3. Results and Discussion

3.1 Dark conductivity

The room temperature dc conductivity of siloxene is about $10^{-18} \, \Omega^{-1} \, cm^{-1}$, as expected for an intrinsic material with an optical band gap of 2.3 eV. At elevated temperatures, e.g. at $T = 500$ K, we find values around $10^{-13} \, \Omega^{-1} \, cm^{-1}$. Plotting the current versus $1000/T$ reveals a thermally activated behavior with an activation energy of ≈ 1 eV. The rather low prefactor $\sigma_0 \approx 10^{-5} \, \Omega^{-1} \, cm^{-1}$ indicates a possible percolation problem. Two typical measurements are shown in Fig. 1. Fig. 1a shows the initial desorption of contaminants which give rise to the high room temperature conductivity in as-prepared samples. Fig. 1b exemplifies the irreversible effect of high-temperature annealing on the conductivity.
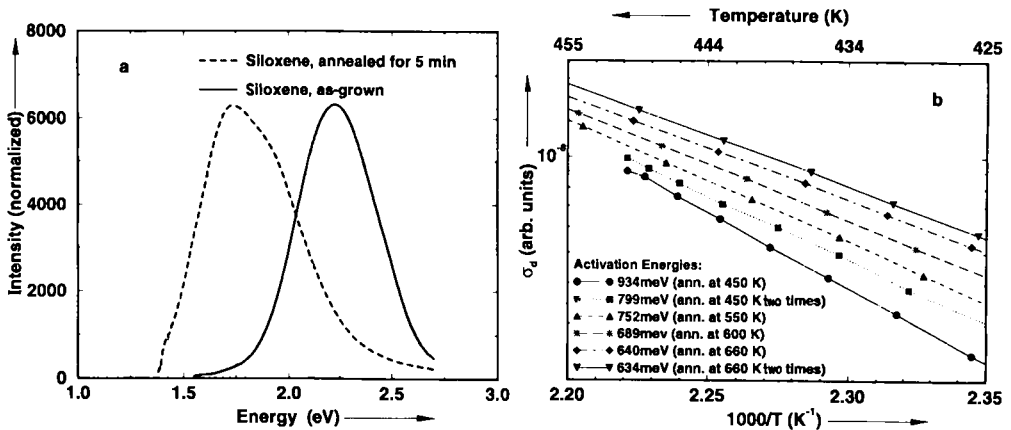

Fig. 2. a) Photoluminescence spectra of thin films of siloxene as-grown and annealed for 5 min at around 350 °C. b) Conductivity of siloxene after thermal annealing at different temperatures. The different curves have been scaled by a suitable factor for better comparison
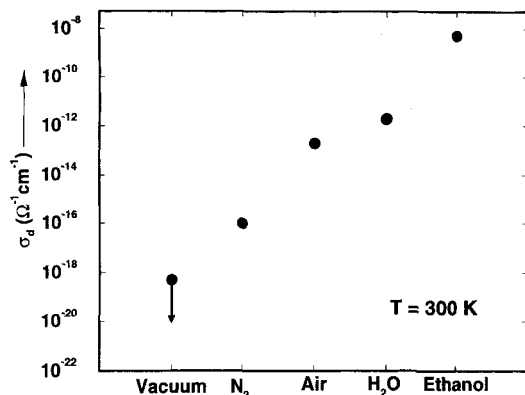
Fig. 3. Dark conductivity of siloxene in different saturated gas atmospheres

Annealing changes the structure of siloxene and reduces its band gap from 2.6 to 2.0 eV [7]. This can be seen both in the photoluminescence (PL) spectra and in the dc conductivity. The PL maximum can be shifted by annealing the sample from about 2.3 to 1.7 eV (Fig. 2a). Simultaneously, the conductivity increases and the conductivity activation energy decreases from ≈ 1 to ≈ 0.6 eV.

In the as-prepared state the conductivity of siloxene depends strongly on the ambient atmosphere. Fig. 3 shows the room temperature conductivities of siloxene in different saturated gas atmospheres. Polar molecules (water, ethanol) increase the conductivity by many orders of magnitude, whereas unpolar gas molecules (N_2) have a much weaker effect.

3.2 Photoconductivity

Fig. 4 shows the dark and the photoconductivity of as-prepared but outgased siloxene as a function of inverse temperature. Below 400 K, the photoconductivity has a weaker temperature dependence than the dark conductivity and exceeds the dark conductivity at room temperature by more than an order of magnitude. According to Fig. 5a, the intensity dependence of σ_{ph} is sublinear and approaches the square-root dependence of bimolecular recombination kinetics at high intensities, with a possible transition to monomolecular
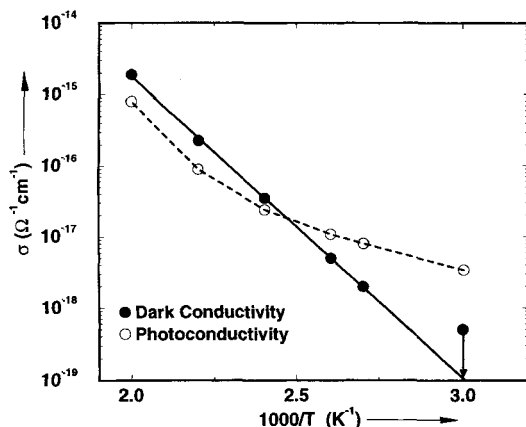

Fig. 4. Dark and photoconductivity of the siloxene sample vs. inverse temperature. The photoconductivity was measured with heat-filtered white light (intensity ≈ 100 mW/cm^2)
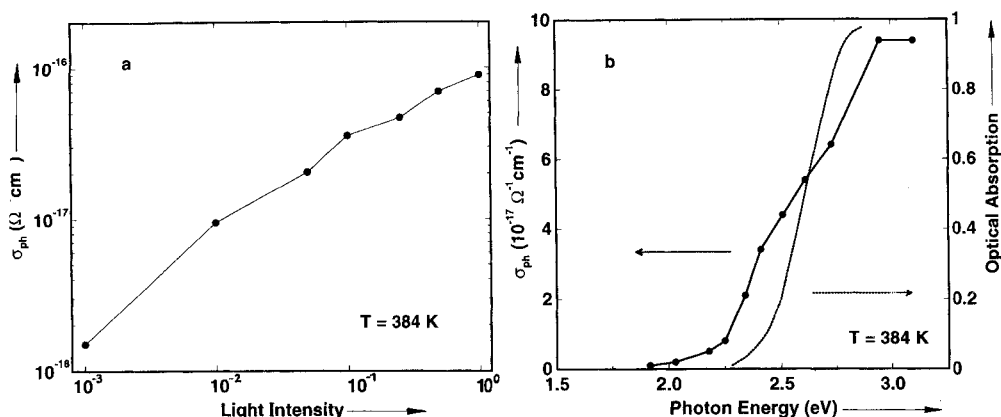
Fig. 5. a) Dependence of the photoconductivity on the incident photon flux. b) Dependence of photoconductivity and optical absorption on the energy of the incident photons

recombination at lower intensities. The dependence on the incident photon energy according to Fig. 5b closely follows the optical absorption.

The experimental results described above are valid both for type-I and type-II samples. A major problem, however, with thin siloxene films on silicon (thickness $\approx 5\ \mu m$) is their mechanical fragility and the occurrence of pinholes. The present work is concentrated on possible ways to overcome these problems.

Acknowledgement

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