



Transport properties and electroluminescence of siloxene

M. Rosenbauer and M. Stutzmann

Citation: Journal of Applied Physics **82**, 4520 (1997); doi: 10.1063/1.366187 View online: http://dx.doi.org/10.1063/1.366187 View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/82/9?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

Correlation between charge transport and electroluminescence properties of Si-rich oxide/nitride/oxide-based light emitting capacitors J. Appl. Phys. **112**, 033114 (2012); 10.1063/1.4742054

Transport properties of annealed CdSe colloidal nanocrystal solids J. Appl. Phys. **92**, 7498 (2002); 10.1063/1.1523148

Light-induced effects on transport in hydrogenated amorphous silicon-sulfur alloys at different temperatures J. Appl. Phys. **91**, 9878 (2002); 10.1063/1.1479477

Optoelectronic and structural properties of amorphous silicon–carbon alloys deposited by low-power electroncyclotron resonance plasma-enhanced chemical-vapor deposition J. Appl. Phys. **85**, 3327 (1999); 10.1063/1.369679

Effects of gallium doping on the properties of amorphous-SiC:H films prepared by magnetron cosputtering J. Appl. Phys. **83**, 2067 (1998); 10.1063/1.366939



Transport properties and electroluminescence of siloxene

M. Rosenbauer^{a)}

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

M. Stutzmann

Walter-Schottky-Institut, Technische Universität München, Am Coulombwall D-85748 Garching, Germany

(Received 18 December 1995; accepted for publication 5 August 1997)

The transport and electroluminescence properties of siloxene (Si₆O₃H₆) in the as-prepared and annealed states are investigated. As-prepared siloxene is found to show a low dark conductivity ($\approx 10^{-19} \ \Omega \ cm^{-1}$) at room temperature which is thermally activated with an activation energy that is approximately half of the optical gap of siloxene ($\approx 2.6 \text{ eV}$). The presence of ambient gases can increase the dark conductivity due to intercalation of gas molecules between the two-dimensional siloxene polymer sheets. The photoconductivity of siloxene is investigated with respect to its spectral and temperature dependences. Electroluminescence of siloxene is found for sufficiently high current levels. © 1997 American Institute of Physics. [S0021-8979(97)09121-4]

I. INTRODUCTION

There is a wide field of possible technical applications for light emitting materials that can be integrated directly on Si electronic devices.¹ Due to its indirect band gap, Si itself cannot be used for light emission. Present activities in Sibased light emitting materials include porous silicon, Si suboxides, semiconductor nanocrystals in a SiO_x matrix, and siloxene. Wöhler's siloxene (Si₆O₃H₆),^{2–5} a twodimensional Si sheet polymer, can be grown epitaxially on Si substrates^{6–8} and is known for its efficient visible photoluminescence. Its transport properties, however, were unknown up to now. In this article, we examine the transport properties of siloxene and present an attempt to achieve electroluminescence (EL) in siloxene.

II. EXPERIMENTAL DETAILS

Siloxene was prepared by the reaction of a 37% HCl solution in water with CaSi2 powder, dissolved in ethanol and then coated on a conducting substrate [a glass plate coated with indium-tin-oxide (ITO)]. After evaporation of the solvent, polycrystalline layers with typical thicknesses between 50 and 200 μ m were obtained and were sandwiched between the ITO plate just described and a second ITOcoated glass plate. Both glass plates were about 8×8 mm in size. The conductivity measurements were performed in vacuum ($<10^{-5}$ mbar) or in well-defined gas atmospheres (H₂O, nitrogen, oxygen, or ethanol). The samples were heated to temperatures up to 600 K to outgas and then cooled to room temperature slowly while measuring the dc conductivity using a Keithley 617 electrometer. The photoconductivity measurements were performed using infrared-filtered light from a halogen lamp with an intensity $\leq 100 \text{ mW/cm}^2$ to avoid heating of the sample. For the EL measurements, a GaAs photomultiplyer with a photon counting system without imaging elements was mounted about 15 cm from the sample. Spectral resolution of either incident or emitted light was achieved by using a set of different cutoff filters. During all measurements, the sample temperature was controlled to within ± 2 K. In addition to the light produced by EL, the high-energy tail of the blackbody radiation of the heated sample was detected by the photomultiplyer. All EL spectra shown in this article are corrected in this respect.

III. RESULTS AND DISCUSSION

A. Dark conductivity

At room temperature, Wöhler siloxene is an insulator. Its dark conductivity in vacuum is $\approx 10^{-19} \Omega \text{ cm}^{-1}$ which is somewhat lower than expected for a three-dimensional, disordered material with an energy gap of 2.6 eV.⁹ The apparent contradiction is resolved by assuming that the conductivity of the single two-dimensional siloxene sheet is much higher; the low conductivity measured is caused, however, by the electrical insulation between the siloxene sheets (percolation). In the powder layer, the siloxene crystallites are tilted with respect to each other and the few direct electrical con-



FIG. 1. I-V characteristic of a layer of Wöhler siloxene pressed between two ITO layers, measured at 400 K in steps of 2 V with a 3 min waiting time at each point. The negative current at V=0 V is due to discharging microcapacitors and shows that an even longer waiting time would be required. At voltages below -60 V, the I-V curve is essentially linear.

© 1997 American Institute of Physics

^{a)}Present address: Groupe de Physique des Solides, Université Paris 6 et Paris 7, Tour 23, 2, Place Jussieu, 75251 Paris Cedex 05, France. Electronic mail: rosenbauer@springer.de



FIG. 2. Dark conductivity of Wöhler siloxene in different saturated gas atmospheres at room temperature. The open points are test measurements using a Teflon layer as the sample and show the noise limit of the system.

tacts between different siloxene sheets are not very likely to form complete current paths from one side of the powder layer to the other, giving rise to a geometric correction factor $\ll 1$. The siloxene–ITO contacts described in Sec. II are characterized by the I-V curve in Fig. 1. Below V=-60 V, this curve is essentially linear and shows that the contacts are ohmic. When recording this measurement, a relaxation time for the current of the order of a few minutes was noted. After shorting the voltage source, the current is inverted and continues for a comparably long time. This can be explained by assuming a large capacitance of the powder sample with a long discharging time due to a high series resistance of the powder material.

The dark conductivity of Wöhler siloxene is very sensitive to ambient gases and can vary by up to 10 orders of magnitude (see Fig. 2). A typical conductivity measurement of siloxene exposed to ambient gases is shown in Fig. 3. At room temperature, the conductivity is high due to gas molecules adsorbed on the large internal surface of the twodimensional sheet polymer siloxene. Such an increase of conductivity is known from amorphous silicon¹⁰ where it



FIG. 3. Arrhenius plot of the conductivity of siloxene powder in saturated gas atmospheres. Adsorbed gas molecules increase the room temperature conductivity and evaporate at medium temperatures. At high temperatures, the conductivity of the siloxene samples increases due to thermal activation.



FIG. 4. Conductivity measurement of Wöhler siloxene in vacuum. At the maximum temperature (350 $^{\circ}$ C), the sample was annealed for about 10 min. The changes of the slope and of the absolute conductivity value show the decrease of the activation energy of siloxene caused by annealing.

was demonstrated that electronic donor states generated by chemisorbed water molecules at the surface increase the conductivity. At temperatures between 100 and 150 °C, these gas molecules desorb and the conductivity approaches the intrinsic value. When further increasing the temperature, the conductivity shows thermally activated behavior. When decreasing the temperature, the conductivity of the outgassed sample first follows a straight line in the Arrhenius plot, then the sample starts again to adsorb gas molecules; finally the conductivity returns to the room temperature starting point. A quantitative evaluation of the slope at high temperatures yields an activation energy of ≈ 1 eV.

Annealing siloxene above 300–400 °C changes its structure and reduces its band gap from 2.6 to 2.0 eV.¹¹ This can be observed independently in photoluminescence, absorption, and conductivity measurements. Figure 4 shows the expected increase of the conductivity⁹ and the decrease of the activation energy after annealing of siloxene powder for 10 min at 350 °C. Table I shows the change of the activation energies of siloxene after annealing in vacuum for approximately 10 min at different temperatures.

B. Photoconductivity

Figure 5 shows the photoconductivity of freshly prepared and of annealed Wöhler siloxene. Both samples were previously outgassed at temperatures above 150 °C. At room temperature, the photoconductivity of as-prepared siloxene

TABLE I. Activation energies of Wöhler-siloxene after 10 min annealing cycles at different temperatures in vacuum. The energy values were determined by fitting exponential functions in the temperature range between 420 and 450 $^{\circ}$ C.

Anneal temperature	Activation energy
	1100 eV
450 K	930 meV
550 K	750 meV
600 K	690 meV
660 K	630 meV

ntent is subject to the terms at: http://scitation.aip.or

M. Rosenbauer and M. Stutzmann 4521



FIG. 5. Arrhenius plot of the photoconductivity of as-prepared and annealed Wöhler siloxene in vacuum. The photoconductivity is generated with white light through an infrared filter. The dark conductivities of the samples are also shown for comparison.

exceeds the dark conductivity by more than one order of magnitude and has a weaker temperature dependence.

At low light intensities, the intensity dependence of the photoconductivity is sublinear and approaches square-root behavior at higher intensities (see Fig. 6) like that usually observed for bimolecular recombination kinetics:¹² at low light intensities, the small number of photocarriers is expected to recombine with the greater number of intrinsic carriers or to be trapped in defect states, leading to a lifetime that is independent of intensity. At higher light intensities, however, photocarriers begin to recombine with each other and therefore the concentration of both reaction partners dependence is expected for the photoconductivity as a function of light intensity.

The spectral dependence of the photoconductivity is shown in Fig. 7. It is mainly determined by the shape of the optical absorption which is included in Fig. 7 for comparison. Wöhler siloxene is light sensitive. Upon irradiation with blue or with ultraviolet (UV) light, its color changes from yellow to white (photooxidation). This change has only a



FIG. 6. Intensity dependence of the photoconductivity. An intensity of 1 corresponds to $\approx 100 \text{ mW/cm}^2$ on the sample.



FIG. 7. Photoconductivity (solid line) in Wöhler siloxene depending on the energy of the incident photons. The optical absorption (dotted line) is drawn for comparison.

minor influence on the spectral shape of the photoluminescence, but it decreases its intensity by a considerable amount.¹³ A similar decrease is also observed in the photoconductivity. Both effects are due to increased nonradiative recombination via deep defects. In electron spin resonance (ESR), these defects have been identified as silicon dangling bonds with a g factor of 2.0047 in as-prepared siloxene. Under illumination, the defect density was found to increase significantly, together with a shift of the g factor to 2.0038, indicating that now at least one oxygen atom is backbonded to the defect carrying silicon atom. This suggests that the degradation mechanism is due to the insertion of oxygen atoms into the siloxene planes. A similar conclusion is also drawn from corresponding studies of the H local vibrational modes.

C. Electroluminescence

Since siloxene shows photoconductivity when excited with photon energies greater than its optical energy gap, it can be assumed that this process can be inverted and that electrically injected conduction band electrons can radiatively recombine with holes. The low conductivity of siloxene, however, makes the straightforward approach of applying a dc voltage to the material to obtain light emission impossible.

Attempts to find EL in siloxene when increasing its conductivity by exposing it to ambient gases (see Fig. 2) were unsuccessful. The increased conductivity contributes very little to photoconductivity or to light emission.

A better way to increase the average current through the siloxene layer without further increasing the voltage follows from the observation of long relaxation times of the current (see discussion of Fig. 1). Applying ac voltages to outgassed siloxene samples in vacuum ($\approx 10^{-5}$ mbar) invokes light emission which can be measured by a photomultiplyer. We note that these very low pressures preclude gas or corona discharge as a possible source of the luminescence. Such discharge effects in air would result in blue light emission as opposed to our EL spectra in the red (see below). Typical EL–voltage dependences are shown in Fig. 8. Because of the



FIG. 8. Intensity of the electroluminescence of Wöhler siloxene vs the effective applied ac voltage. The lines are proportional to the fourth power of the voltage.

low currents, it was not possible to measure the value and the phase of the current with respect to the driving voltage.

The ac conductivity is not restricted to the few complete current paths through the whole powder layer. Insulated carriers which are hopping forward and backward under the influence of the electric field contribute to the ac conductivity. This kind of hopping conductivity in amorphous materials has a frequency dependence that can be approximated by

$$\sigma(\omega) \propto \omega^s. \tag{1}$$

For frequencies in the kHz regime, values for *s* of about 0.6 are expected.¹² Assuming that the light intensity is proportional to the ac current, Fig. 9 confirms that Eq. (1) is valid and that the current is mainly limited by hopping.

The spectrum of the EL of siloxene is shown in Fig. 10. In contrast to the photoluminescence (PL) spectrum, its peak is in the infrared and the peak position cannot be measured with a GaAs photomultiplyer. Hence Fig. 10 only shows the PL spectrum above ≈ 1.4 eV. Supposedly the radiative recombination of the carriers involves defect states within the energy gap. The spectrum of annealed Wöhler siloxene is



FIG. 9. Intensity of the electroluminescence of Wöhler siloxene vs the frequency of the applied ac voltage. Independent of the voltage, the intensity follows a $\nu^{0.6}$ law.



FIG. 10. Spectrum of the electroluminescence (solid line) of Wöhler siloxene at 384 K. The applied ac voltage is 100 V with 20 kHz. The points show the EL intensities measured with different cutoff filters. These values were corrected for the photomultiplyer response. The spectrum is obtained numerically by taking the derivative of the measured values.

slightly redshifted with respect to the spectrum shown in Fig. 10. The conductivity of annealed siloxene can be high enough to measure EL even with dc voltages. In this case, the current can be measured and the quantum efficiency of the EL is greater than 10^{-3} %.

For applications, the conductivity of siloxene needs to be increased. Since almost perfect epitaxial growth of siloxene planes on Si(111) surfaces has already been demonstrated,^{8,14} it seems possible to channel the electric current through siloxene layers aligned parallel to each other if a technical solution for obtaining electrical contacts to both ends of the layers could be found.

IV. CONCLUSION

The conductivity of siloxene is thermally activated (E_{σ} $\approx 1 \text{ eV}$) and has low room temperature values $(\approx 10^{-19} \ \Omega \ cm^{-1}$ probably due to insufficient electrical contacts between different fragments of randomly oriented twodimensional siloxene sheets. Adsorbed gas molecules can increase the dark conductivity by many orders of magnitude but do not significantly change the photoconductivity or the EL. The photoconductivity at low light intensities is mainly limited by recombination of photocarriers with intrinsic carriers, and at higher intensities by recombination of the photocarriers with each other. The ac conductivity of siloxene is higher than the dc conductivity and shows a frequency dependence typical of hopping conduction in amorphous semiconductors. The EL spectrum has its peak at energies far below the energy gap. This could be explained by defect states within the energy gap taking part in the radiative recombination processes.

ACKNOWLEDGMENTS

The authors thank U. Dettlaff-Weglikowska for preparing some of the Wöhler siloxene samples and H. Hirt and G. Schneider for technical support. Stimulating discussions with

128.138.73.68 Opt Mon 22 Dec 2014 21:20:21

J. Weber and S. Finkbeiner are gratefully acknowledged. This work was supported by the European Union under Contract No. Copernicus 93-7839.

- ¹L. Brus, J. Phys. Chem. 98, 3575 (1994).
- ²F. Wöhler, Lieb. Ann. **127**, 257 (1863).
- ³E. Hengge, G. Olbrich, and E. Georgiadou, Monatsh. Chem. **99**, 686 (1968).
- ⁴H. Kautsky, Z. Anorg. Chem. **117**, 209 (1921).
- ⁵A. Weiss, G. Beil, and H. Meyer, Z. Naturforsch. B 34, 25 (1979).
- ⁶M. Rosenbauer, M. S. Brandt, H. D. Fuchs, A. Höpner, A. Breitschwerdt, and M. Stutzmann, in *Optical Properties of Low-Dimensional Silicon Structures*, edited by D. C. Bensahel (Kluwer Academic, Dordrecht, The Netherlands, 1993), p. 43.

- ⁷M. S. Brandt, A. Breitschwerdt, H. D. Fuchs, A. Höpner, M. Rosenbauer, M. Stutzmann, and J. Weber, Appl. Phys. A 54, 567 (1992).
- ⁸K. Huang, M. Rosenbauer, and J. Zegenhagen, Bull. Am. Phys. Soc. (1995).
- ⁹R. A. Street, *Hydrogenated Amorphous Silicon* (Cambridge University Press, Cambridge, 1991).
- ¹⁰B. Aker, Philos. Mag. B 55, 313 (1987).
- ¹¹P. Deák, M. Rosenbauer, M. Stutzmann, J. Weber, and M. S. Brandt, Phys. Rev. Lett. **69**, 2531 (1992).
- ¹²N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1979).
- ¹³W. Wang, H. C. Chen, and X. L. Zheng, Mater. Lett. 14, 343 (1992).
- ¹⁴M. Rosenbauer, Dissertation, Technische Universität München, 1995.