

Local and electronic structure of siloxene

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Silicon L_{2,3} x-ray emission spectra (XES) of siloxene powder samples prepared according to Wöhler and Kautsky (Wöhler and Kautsky siloxene) are presented. The results are compared with the Si L_{2,3} spectra of the reference compounds *a*-Si, *c*-Si, SiO₂, and SiO_x. A close similarity of the electronic structure of Wöhler siloxene to that of *a*-SiO_{0,43} : H and of Kautsky siloxene to that of *a*-SiO_{0,87} : H is found. We determine the number of oxygen atoms per Si atom at ~0.5 in Wöhler siloxene and ~0.8 in Kautsky siloxene. The relative concentrations are in good agreement with the results of infrared absorption measurements on the same samples.

I. INTRODUCTION

Light-emitting, silicon-based materials are very attractive for an integration with silicon microelectronics in optoelectronic devices.¹ Crystalline silicon (c-Si) is not suited for visible light emission, due to the small indirect band gap of about 1.1 eV. An efficient visible luminescence at room temperature from Si is, however, possible by drastic changes in the band structure. Different methods were pursued in the past to modify the band structure of c-Si: amorphous Si alloys with a high degree of structural disorder $(a-SiH_x, a-SiC_x, a-SiC_x)$ a-SiO_x, a-SiN_x), quantum confinement in crystallites of 10-20 Å [porous silicon (*p*-Si)], or by the reduction of the dimensionality in silicon backbone materials [e.g., planar silane $(SiH)_n$, linear polysilanes $(SiH_2)_n$, siloxene (Si₆O₃H₆)_n]. Siloxene exhibits a strong visible (yellowgreen) photoluminescence^{2,3} and it is considered as an alternative material for Si-based luminescent devices. Siloxene has attracted considerable interest due to the controversial discussion on the origin of the strong visible photoluminescence from porous silicon. It has been proposed that the visible luminescence of porous silicon originates from a siloxene contamination.^{4,5}

Two ideal modifications of siloxene are shown schematically in Fig. 1. On the left-hand side of the Si-planar structure $[Si_6H_{6-x}(OH)_x]_n$ for x = 3 is given. This modification consists of planes in which the silicon atoms form covalently bonded puckered layers similar to the (111) plane of *c*-Si and OH groups. The crystal

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structure of Si planar is verified experimentally only for samples which were prepared according to the procedure given by Wöhler⁶ (so-called "as prepared" Wöhler siloxene). On the right-hand side of Fig. 1 a Si-ring modification of siloxene is shown ($[Si_6H_6O_{2x/2}]_n$). The crystal structure of this siloxene modification is not determined up to now because the preparation method according to Kautsky yields an x-ray amorphous product which contains also other siloxene modifications. Only theoretical calculations and qualitative arguments for the structural arrangements can be given for this Si-ring



FIG. 1. Structural models of two modifications of siloxene (Si₆O₃H₆). Left: Si planes terminated by H and OH groups; right: Si₆ rings interconnected via oxygen bridges and terminated by hydrogen. Large atoms symbolize Si, small dark atoms hydrogen, and medium size atoms oxygen.

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modification. In the present paper we report on a study of the local structure of Si atoms in Wöhler and Kautsky siloxene powders by x-ray emission spectroscopy (XES).

II. EXPERIMENTAL

Wöhler and Kautsky siloxene powder samples were prepared according to the optimized synthesis described in Ref. 14. The chemical analysis yields the ratio Si: H:O = 6.00:5.58:2.96, which is close to the idealized formula Si₆H₃(OH)₃ determined.

Si L_{2,3} (3s3d $\rightarrow 2p$ transition) x-ray emission spectra (XES) were measured by using a small-spot x-ray emission spectrometer with a diffraction grating (N = 600 lines/mm, R = 2 m) and electron excitation.⁹ The spatial resolution was 4–5 μ m and the energy resolution about 0.4 eV. The samples under investigation formed the target of the x-ray tube which was operated at 6 keV and 300 nA.

III. RESULTS AND DISCUSSION

Silicon L_{2,3} x-ray emission spectra correspond to radiative transitions between the valence states and the Si 2p core level which can be ionized by electron or photon excitation (in our experiments electron excitation was used). As a result of the dipole selection rules the Si L_{2.3} XES probes the (3s + 3d) partial density of states (DOS) localized at the silicon atoms. It was shown in our previous papers (see Refs. 9-11) that the site projected (3s + 3d) DOS extracted from Si L_{2.3} XES is very sensitive to the chemical bonding and that the fine structure and energy position of the spectral features are sufficiently different in pure silicon and silicon compounds to distinguish between them. On the other hand, the x-ray transition is localized within the limits of the first coordination sphere of the emitting atom and Si L_{2,3} XES is sensitive to the short order (coordination number, bond length, etc.). Therefore, by using XES it is possible to distinguish the amorphous and crystalline state of pure silicon and to study changes in the local environment of the emitting atom.

The results of the XES measurements on Wöhler and Kautsky siloxene are shown in Fig. 2 together with spectra of the reference materials (*a*-Si, *c*-Si, and SiO₂). Obviously the XES of siloxenes differs from that of *c*-Si. The electronic structure of both Kautsky and Wöhler siloxene powder samples reflected in the XES resemble that of amorphous silicon, although the Kautsky siloxene shows also a resemblance to SiO₂, due to the double peak structure in the emission spectrum. Our data are in agreement with those Si 1*s* and Si 2*p* x-ray absorption measurements,¹² where the siloxene spectrum was simulated as a superposition of the SiO₂ and amorphous silicon spectra. The Si L_{2,3} spectrum of amorphous (hydrogenated) silicon (*a*-Si) exhibits a



FIG. 2. Si $L_{2,3}$ XES of Wöhler and Kautsky siloxenes in comparison with spectra from reference materials (*c*-Si, *a*-Si, SiO₂).

broad peak (90.4 eV) and a shoulder on the high photon energy side whereas the spectrum of Wöhler siloxene has an emission maximum which is slightly shifted to $E \sim 89.5 \text{ eV}$ and a broad shoulder at a slightly lower energy than that occurring in a-Si. Due to the high electronegativity of the oxygen, two different bonding states for Si atoms in the structural units H-Si-Si₃ and HO-Si-Si₃ of Wöhler siloxene are expected. However, features characteristic for Si-Si bonds dominate in the spectral region 86-99 eV. It seems that the tetrahedral coordination of Si in HO-Si-Si₃ is not changed significantly by the presence of oxygen in Wöhler siloxene. It is interesting to note that a similar spectrum is observed in amorphous hydrogenated silicon oxide alloy SiO_{0.47}: H¹³ (see the comparison in Fig. 3), suggesting the same local s-, p- and d-like symmetries of valence electrons creating Si-O bonds in both materials.

The Si L_{2,3} spectrum for Kautsky-siloxene consists of two broad maxima at 89 and 94 eV of approximately equal amplitude. According to Ref. 13, the intensity ratio of these peaks is similar to those of the SiO_{0.83} : H alloy (Fig. 3). The double peak structure in the XES of Si in the Kautsky siloxene can be understood from the band structure calculation of crystalline SiO₂¹³ and can be interpreted as a result of Si(3s3d)–O(2p) hybridization with different weights of the Si(3s) and Si(3d) states. The intensity ratio of the two peaks of Si L_{2,3} XES in

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FIG. 3. The comparison of Si $L_{2,3}$ XES of Wöhler and Kautsky siloxenes with spectra of $SiO_{0.47}$ and $SiO_{0.83}.^{13}$

Wöhler and Kautsky siloxene is different and follows the variation of the oxygen content.

We conclude therefore that the appearance of the two peaks in the spectra of siloxene is directly associated with the oxygen atoms nearest to the emitting silicon. The intensity of the peaks and their position is determined by the relative concentration of oxygen atoms per Si atom: an increasing number of Si–O bonds per Si atom increases the intensity of the peaks formed by Si(3s3d)–O(2p) electrons.

The comparison of the siloxene spectra with the XES of a-SiO_x: H ($0 \le x \le 2.2$)¹³ reveals the close similarity of the electronic structure of Wöhler siloxene to a-SiO_{0.43}: H and of Kautsky siloxene to a-SiO_{0.87}: H. From the similarity in the spectra, we conclude that the number of oxygen atoms per Si atom is ~ 0.5 in Wöhler and ~ 0.8 in Kautsky siloxene powders. The relative oxygen concentrations derived from the comparison of the XES spectra can be compared to the results of the infrared absorption measured on the very same samples.¹⁴ From the infrared absorption spectra we determine the relative intensities of different hydrogen modes. For the Kautsky siloxene powder sample we find H-Si-O₃ (20.5%), H-Si-(SiO₂) (18.8%), and H-Si-(Si₂O) (60.7%). The first two modes belong to the nonideal composition of the sample. Apparently, the preparation according to Kautsky leads, in addition to the ideal Si-ring structure shown in Fig. 1 (right) with the infrared active H-Si-(Si₂O) group, to structures which contain $H-Si-O_3$ and $H-Si(SiO_2)$ groups. Taking the above relative concentrations, one can attribute about 0.8 oxygen atoms per Si atom. For Wöhler siloxene only two hydrogen modes can be detected: H-Si-(Si₃) (50%) and $H-O-Si-(Si_3)$ (50%). This leads to 0.50 oxygen atoms per Si atom as expected for the ideal Si-plane modification shown in Fig. 1 (left). The relative concentrations derived from the infrared absorption are in excellent agreement with the XES data.

IV. CONCLUSION

Silicon L_{2,3} x-ray emission spectra from Wöhler and Kautsky siloxene powder samples are presented and compared to spectra of the reference compounds a-Si, c-Si, SiO_2 , and SiO_x . We find a close similarity of the electronic structure of Wöhler siloxene to that of a-SiO_{0.43} : H and of Kautsky siloxene to that of $a-SiO_{0.87}$: H. The number of oxygen atoms per Si atom is derived from a comparison with the reference samples. One Si atom binds roughly 0.5 oxygen atoms in Wöhler siloxene and roughly 0.8 oxygen atoms in Kautsky siloxene. The ratio of oxygen to Si atoms is in good agreement with the results from the infrared spectra. Our results confirm that Wöhler-siloxene samples contain only the Si-plane modification, whereas Kautsky-siloxene samples are mixtures of several modifications with a dominant contribution from the Si-ring modification.

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