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ATR-FTIR Experiments with Chlorosilanes

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Abstract. OH groups on the surface of semiconductors (SC) such as Si, Ge, TiO_2, SnO_2 react with Cl$-$Si groups to give stable SC$-$O$-$Si bonds. ATR-FTIR is applied to study the infrared spectra of adsorbed $H_8Si_8O_{12}$ on ZnSe and $Cl_8Si_8O_{12}$ which has reacted with the surface $-$OH group of Ge. A comparison is made with the spectra of the free molecules.

Key words: cage molecules, silsesquioxanes, surface modification, infrared spectroscopy, ATR spectroscopy.

One highly successful form of surface modification is silanization. A silane containing a hydrolytically unstable bond will react with a surface OH group to form a silyl ether bond to the substrate [1]: $-OH + X-Si- \rightarrow -O-Si- + HX$. FTIR spectroscopy has proved to be very useful in providing information on such surface layers [2]. If the substrate is a sufficiently transparent crystal, very interesting studies can be made by means of the attenuated total internal reflection (ATR) spectroscopy [3]. ATR-FTIR spectroscopy can be applied to follow adsorption kinetics or reaction kinetics of surface modification [4] and to study photochemical, photoelectrochemical and electrochemical reactions on semiconductor surfaces.

We report first experiments with $R_8Si_8O_{12}$ (R = H, Cl) molecules. The synthesis of these molecules has been described in ref. [5]. Its structure is shown in Fig. 1 and the infrared spectrum of $H_8Si_8O_{12}$ is drawn in Fig. 2. Due to the O_h symmetry of this molecule, only the 6 $T_{1u} \leftarrow A_{1g}$ transitions are infrared active. We name them ν_1, ν_2, ν_3, ν_4, ν_5, ν_6, where ν_1 corresponds to the Si$-$H stretching mode, ν_3 to the Si$-$H bending mode and ν_2 is the Si$-$O stretching vibration. The assignment of the other frequencies is not yet definitive. From 4000 to 700 cm^{-1}, the spectrum was measured in CCl_4, and from 700 to 40 cm^{-1} in a polyethylene wafer at room temperature.

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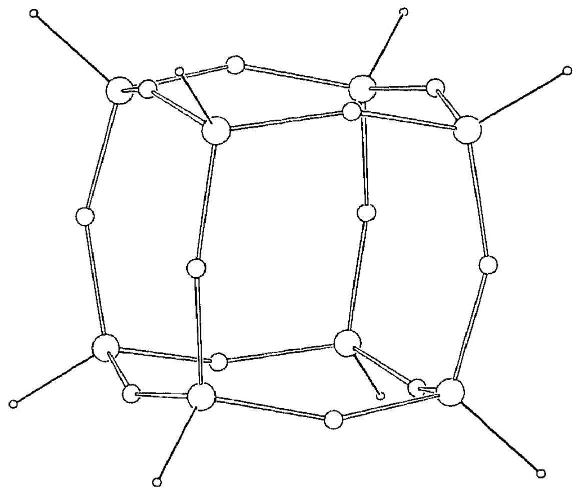

Fig. 1. Structure of $R_8Si_8O_{12}$

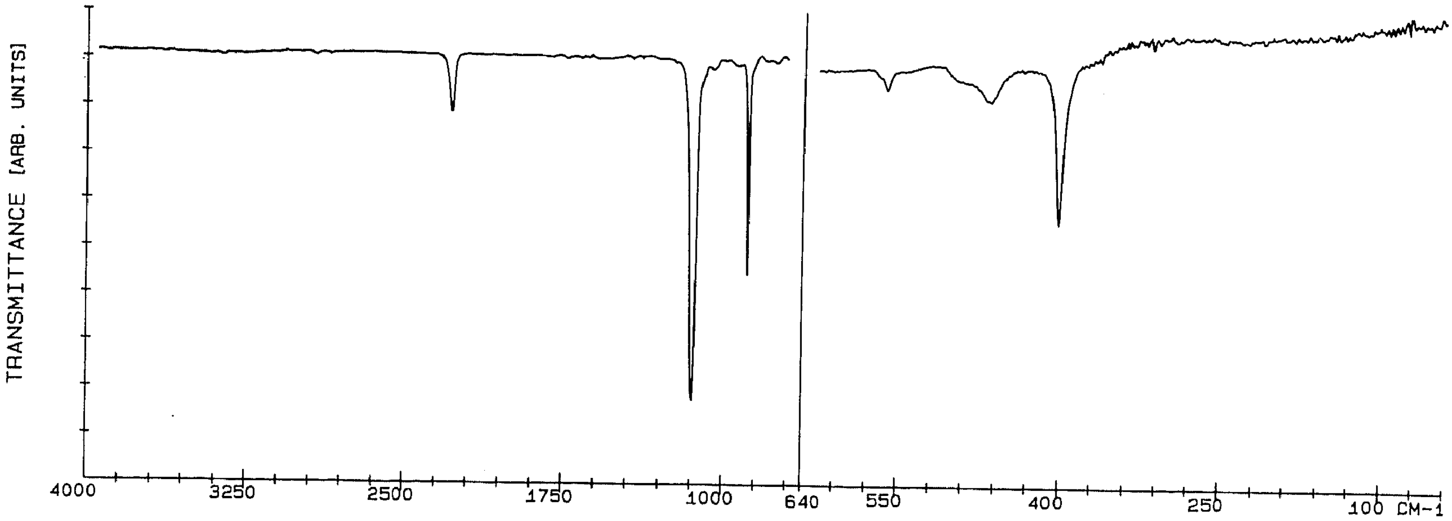

Fig. 2. Infrared spectrum of $H_8Si_8O_{12}$ from 4000 to 40 cm^{-1}. In the range from 4000 to 700 cm^{-1} in CCl_4 and below in a polyethylene wafer

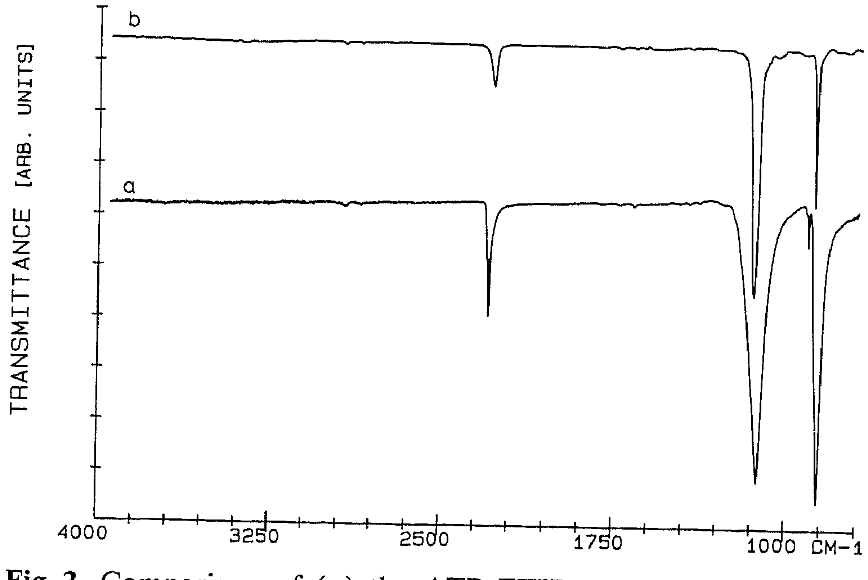

Fig. 3. Comparison of (*a*) the ATR-FTIR spectrum of $H_8Si_8O_{12}$ on ZnSe and of (*b*) the spectrum in CCl_4 from 4000 to 700 cm^{-1}

Fig. 4. ATR-FTIR spectrum of $Cl_8Si_8O_{12}$ on Ge; (*a*) after reacting with the surface OH groups; (*b*) after exposure to water

The qualitative features of both spectra are the same, however, the origin of the broadening and the small peak at 911 cm^{-1} observed on the crystal is not yet clear and needs further investigation.

In Fig. 4 we show the ATR spectrum of the $Cl_8Si_8O_{12}$ on Ge after reacting with the surface OH groups. The Ge crystal was first washed with EtOH and CCl_4, dried under vacuum and plasma and cleaned for 20 min in an air plasma at 4 Pa. The reaction was carried out by immersing the SC crystal in a CCl_4 solution of $Cl_8Si_8O_{12}$ at 80°C for 12 h. After this time the crystal was rinsed with CCl_4. Spectra were taken (*a*) immediately after this procedure and (*b*) after exposing the "reacted" crystal to water for 5 min. In (*b*) a new band at 951 cm^{-1} is formed. This implies that the band at 951 cm^{-1} is the SiO stretching mode of the free SiOH groups.

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