Atomic Structure of SiS_2 and $SiSe_2$ Glasses

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The first study of the atomic structure of Si chalcogenide glasses is reported. The Raman spectra are remarkably simple and can be understood in terms of the vibrations of a bitetrahedral $Si_2(X_{1/2})_8$ (X=S, Se) unit. The present results represent the most compelling evidence for medium-range order and a molecular-cluster description of a compound amorphous semiconductor.

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One of the important fundamental problems in condensed matter physics is the nature of the atomic structure of inorganic covalently bonded glasses. The special focus of previous work in this area has been the glassy systems $Ge(S,Se)_2$ and $As_2(S,Se)_3$.[1-5] Although there is strong evidence for the existence of short-range order in covalent glasses such as $Ge(S,Se)_2$[3] and metallic glasses such as La-Al-Ga,[6] convincing evidence for medium-range order in glasses is lacking. Some suggestions concerning the medium-range order in $GeSe_2$[1,3] have been made; however, at present these remain highly controversial. In this Letter, the results of the first study of the vibrational spectra of crystalline and glassy SiS_2 and $SiSe_2$ are presented. The present results represent the most direct evidence for medium-range order and a molecular-cluster description of a compound amorphous semiconductor.

In the systems $As_2(S,Se)_3$ and $Ge(S,Se)_2$, Phillips[7] has suggested that the glass-forming abilities of these alloys are related to the presence of donor and acceptor clusters. These clusters are formed on the basis of the principle of broken chemical order. For example, the acceptor clusters are proposed to be bordered by chalcogen dimers and are therefore chalcogen rich in composition.[7] In contrast to these elaborate descriptions, the present study reveals that the characteristic molecular cluster of the Si-based glasses has the same composition as the crystalline compound.

Melts of SiS_2 and $SiSe_2$ were prepared by sealing the proper amounts of the elements in an evacuated fused silica tube and heating to 1100 °C. The starting materials were 99.999% pure, the typical size of the melts was 1 g, and the compositions reported here are the nominal ones. After alloying at 1100 °C for 3 d, the melts were quenched in water. Defect-free, slightly yellow glasses were formed for both SiS_2 and $SiSe_2$.

Differential scanning calorimetric measurements of the as-prepared samples confirm the glassy nature of these materials. The glass transition temperature (T_g) and crystallization temperature (T_x) values are $T_g = 453\,°C$, $T_x = 542\,°C$ for SiS_2 and $T_g = 460\,°C$, $T_x = 610\,°C$ for $SiSe_2$.

Room-temperature Raman spectra of the glassy and crystalline samples were taken with a Spex Ramalog 4-1401 double monochromator equipped with a cooled photomultiplier. Typical spectra were recorded using 20 mW of power at the sample with the 5145-Å line of an argon-ion laser and six-wave-number resolution. The measurements were performed with the samples sealed in fused silica tubes or in an Ar-filled sample chamber.

Typical Raman spectra of glassy and crystalline samples are shown in Figs. 1 and 2. The crystalline spectra display very sharp lines and high-resolution spectra indicate that the linewidths are on the order of 5 cm^{-1}. The spectra of the glassy samples had somewhat broader linewidths (about 14 cm^{-1}). In both the SiS_2 and $SiSe_2$ cases there is a one-to-one correspondence between the lines observed in the crystalline samples and those found in the spectra of the glasses. The results of high-resolution (1-cm^{-1} resolution) scans of these samples are listed in Tables I and II. The one significant difference between the spectra of a-SiS_2 and a-$SiSe_2$ is that the peak near 375 cm^{-1} in a-SiS_2 is split into two peaks while the corresponding peak in a-$SiSe_2$ (204 cm^{-1}) is unsplit.

Studies of the compositional dependence of the Raman spectra for the glassy systems Si_xS_{1-x} and Si_xSe_{1-x} have been completed. An important observation from these studies in the context of the present work is that the relative intensities of the peaks that will later be associated with $Si(S,Se)_2$ units are independent of composition. This is in sharp contrast to previous work on the isoelectronic glasses GeS_2 and $GeSe_2$, where an unusual dependence on composition was reported for the so-called A_1 companion line[1] in the Raman spectra.

In previous investigations of crystalline and glassy $GeSe_2$ it has been observed that the Raman

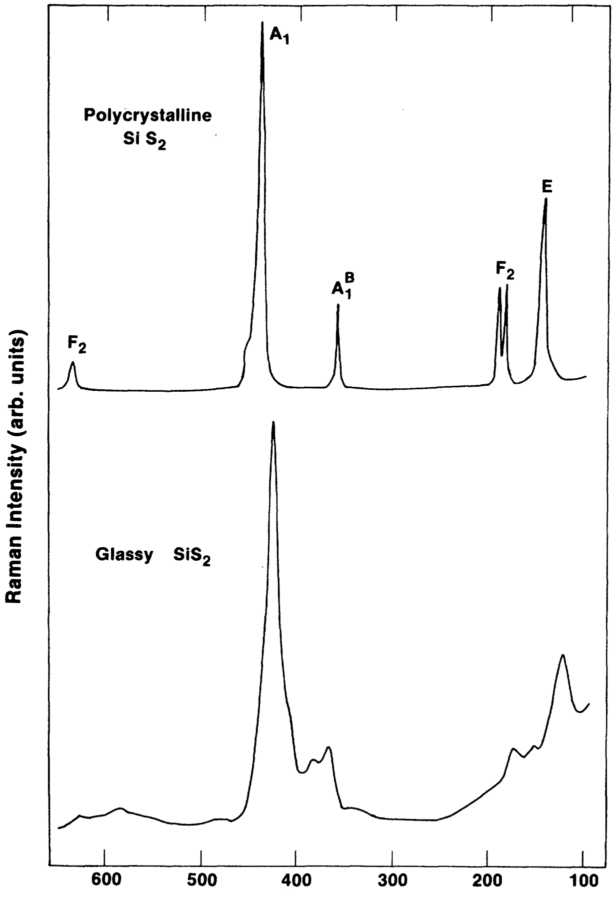

FIG. 1. Raman spectra of polycrystalline and glassy SiS_2. See Table I for the identifications and polarizations of the lines.

spectra are dominated by the normal modes of $Ge(Se_{1/2})_4$ tetrahedra.[2] There are four Raman actives modes in a tetrahedral unit (symmetry A_1, E, F_2, and F_2) with the most symmetric vibration (A_1) generally having the greatest intensity (i.e., largest Raman cross section). The

TABLE I. Raman measurements and identification of vibrational modes of amorphous and crystalline SiS_2.

a-SiS_2 (cm^{-1})	c-SiS_2 (cm^{-1})	Mode
121 (U)[a]	138	E $Si(S_{1/2})_4$
174 (U)	175,181	F_2 $Si(S_{1/2})_4$
367,381 (P)	351	A_1^B $Si_2(S_{1/2})_8$
427 (P)	430	A_1 $Si(S_{1/2})_4$
625 (U)	625	F_2 $Si(S_{1/2})_4$

[a] P, polarized; U, unpolarized.

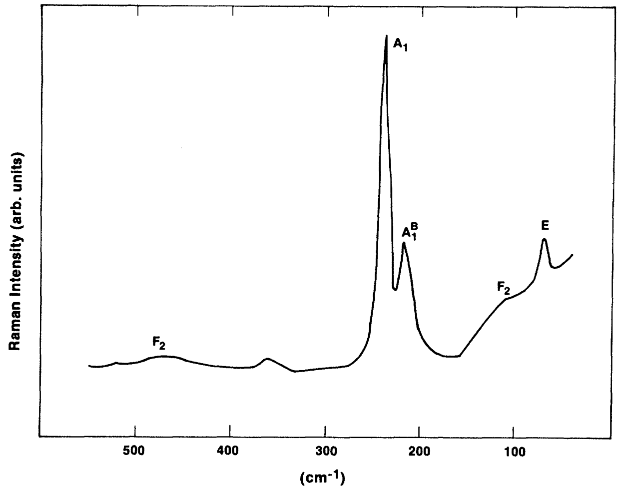

FIG. 2. Raman spectra of glassy $SiSe_2$. See Table II for the identifications and polarizations of the lines.

identifications of the various Raman lines are listed in Tables I and II based on comparisons with the observed spectra of $SiCl_4$ and $SiBr_4$, the polarization measurements, and the results of a molecular-cluster calculation.[4] The molecular-cluster calculation uses the observed modes of the Si-halogen compounds and corrects for the differences in masses and bond strengths for the chalcogenide cases.

An intriguing feature of the Raman spectra of SiS_2 and $SiSe_2$ is the presence of the line referred to as A_1^B in Tables I and II. This line is not a normal mode of a SiX_4 tetrahedral unit and occurs with approximately the same relative intensity in both the glassy and the crystalline forms. The microscopic origin of this line can be inferred from a comparison of the S and Se spectra and the known crystal structure of $Si(S,Se)_2$. Expressing the Raman frequencies for the glasses and

TABLE II. Raman measurements and identification of vibrational modes of amorphous and crystalline $SiSe_2$.

a-$SiSe_2$ (cm^{-1})	c-$SiSe_2$ (cm^{-1})	Mode
68 (U)[a]	82	E $Si(Se_{1/2})_4$
110 (U)	111,122	F_2 $Si(Se_{1/2})_4$
216 (P)	204	A_1^B $Si_2(Se_{1/2})_8$
242 (P)	243	A_1 $Si(Se_{1/2})_4$
350 (U)	345,355	...
465 (U)	512	F_2 $Si(Se_{1/2})_4$

[a] P, polarized; U, unpolarized.

crystals as $\nu(\mathrm{SiS_2}) = \alpha\nu(\mathrm{SiSe_2})$, α is found to be approximately 1.75 for both the A_1 and A_1^B lines. This value is in excellent agreement with that obtained by a molecular-cluster calculation assuming that the microscopic origin of this mode involves only the symmetric stretch of chalcogens atom away from Si atoms ($\alpha = 1.77$). Further evidence for this assignment comes from the observation that the A_1^B modes are polarized and therefore represent symmetric vibrations. The crystal structure of SiS_2 and $SiSe_2$ is $C42$ type[8] in which there are two parallel chains of edge-sharing tetrahedra per unit cell. The basic repeating unit of the chains is a bitetrahedral unit of composition $\mathrm{Si_2}(X_{1/2})_8$. There are two candidates for symmetric vibrations involving only the motion of the chalcogenide atoms in these chains. One is the A_1 mode of $\mathrm{Si}(X_{1/2})_4$ tetrahedra. The other is the symmetric vibration of the four outer chalcogens of the bitetrahedral units. Since the A_1 mode is expected to have the largest Raman cross section and to have approximately the same frequency in the crystals and glasses, the identification of these modes in Tables I and II is clear. The modes denoted A_1^B therefore represent the symmetric vibrations of the four outer chalcogens of the bitetrahedral units. The presence of A_1^B lines in the Raman spectra of the corresponding glasses with the same relative intensity as in the crystals is direct evidence of medium-range order. In particular, the medium-range order of the glasses consists of chains of edge-sharing tetrahedra.

In the crystalline compounds, the chains of tetrahedra are held together by van der Waals bonding at a distance of about 6–7 Å. Neutron-diffraction measurements of a-$SiSe_2$ have revealed an anomalous first sharp diffraction peak at 1 $\mathrm{\AA}^{-1}$, similar to that observed in a-P, a-As, a-Sb, a-$GeSe_2$, and a-As_2S_3.[7] There has been considerable controversy concerning the relation of such first diffraction peaks to the structure of the material.[9] Two common suggestions are that the peaks result from layering or from the presence of molecular clusters. For the Si glasses of this study, a layered structure is not likely and a more plausible explanation is that the first diffraction peak indicates the presence of molecular clusters. An important question regarding the network of edge-sharing tetrahedral chains is the length of the chains. In principle it could range from isolated bitetrahedral units to essentially infinite chains like that of the crystalline phases. The presence of the anomalous first sharp diffraction peak in the neutron-diffraction data of a-$SiSe_2$ implies that the chains are extended units. The major difference between the atomic structure of the crystalline and glassy phases of these materials is the nature of the packing of the chains of tetrahedra. In the crystalline compounds the chains are essentially infinite in length and parallel. In contrast to this, the chains are expected to be randomly oriented in the glasses with the average chain-chain distance approximately the same as in the crystalline compounds.

The present study provides the first direct evidence for substantial medium-range order in an amorphous semiconductor. The $\mathrm{Si(S,Se)_2}$ glasses are composed of extended chains of edge-sharing tetrahedra with the composition of the molecular clusters being the same as the crystalline compounds. This description is in contrast to the ideas proposed by Phillips[7] for broken chemical order in $\mathrm{As_2(S,Se)_3}$ and $\mathrm{Ge(S,Se)_2}$ glasses. The relatively simple structure of the Si-based glasses permits a variety of new experiments. For example, results of investigations on the mechanisms of isoelectronic substitution in glasses will be reported soon.

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