Raman-effect studies of Si_xS_{1-x} glasses

M. Tenhover, M. A. Hazle, and R. K. Grasselli

Department of Research and Development, The Standard Oil Company (Ohio), 4440 Warrensville Center Road,
Warrensville Heights, Ohio 44128

The atomic structure of Si_xS_{1-x} glasses is investigated by the use of Raman spectroscopy. The compositional dependence of the microstructures of these glasses can be conveniently divided into three regions. At SiS_2, the glassy structure is composed of randomly oriented edge-sharing $Si(S_{1/2})_4$ tetrahedral chains. Excess Si ($x > \frac{1}{3}$) is accomodated in the glasses as ethanelike S_3-Si-Si-S_3 units. For Si-poor glasses, an unusual compositional dependence is observed of the Raman mode associated with the extended SiS_2 edge-sharing tetrahedral chains. This behavior is related to the emergence of isolated $Si(S_{1/2})_4$ tetrahedral units as the Si content of the glasses is decreased below $x = 0.25$. In the Si-poor glasses, S_8 units, fragments of S_8 units, isolated $Si(S_{1/2})_4$ tetrahedral units, and SiS_2 units are observed. The present work is the first to address the question of the microstructure of chalcogenide-rich Si glasses.

I. INTRODUCTION

The atomic structure of Si-based chalcogenide glasses has recently been the subject of considerable interest. This interest stems from the relatively simple atomic structure of these glasses compared to Ge-based glasses and the fact that Raman spectroscopy provides direct evidence for medium-range order. Previous work has focused on the atomic structure of glassy SiS_2 and $SiSe_2$,[1] the compositional dependence of the structure of Si_xSe_{1-x} glasses $(0.30 \leq x \leq 0.40)$,[2] and the question of isoelectronic substitution in $(Si_xGe_{1-x})S_2$ glasses.[3] This work is concerned with the atomic structure of Si_xS_{1-x} glasses in the range $0.05 \leq x \leq 0.40$. This includes chalcogenide-rich glasses $(x < \frac{1}{3})$, which have not been investigated in previous studies.

II. EXPERIMENTAL PROCEDURE

Bulk glasses (1–2 g) of Si_xS_{1-x} were prepared by water quenching the molten alloys. The starting materials (99.999% pure Si and S) were vacuum sealed in fused silica tubes and alloyed at 1100 °C for 4–7 days. Water quenching the samples of this study $(0.05 \leq x \leq 0.40)$ led to the formation of defect-free glasses for $0.05 \leq x \leq 0.35$. For $x > 0.35$, the as-quenched samples were inhomogeneous, consisting of pieces of undissolved Si. Room-temperature Raman spectra of the Si_xS_{1-x} samples were taken with the samples sealed in fused silica tubes. The experimental procedure is the same as that described in Ref. 2. The compositions reported here are the nominal ones determined simply by the relative amounts of the two components initially sealed in the fused silica tubes.

III. EXPERIMENTAL RESULTS

The Raman spectra of a few of the samples of this study are shown in Figs. 1 and 2. Sharp molecularlike

modes are observed for all compositions. The discussion will begin with an examination of the spectrum of SiS_2 followed by Si-rich $(x > \frac{1}{3})$ and Si-poor $(x < \frac{1}{3})$ glasses.
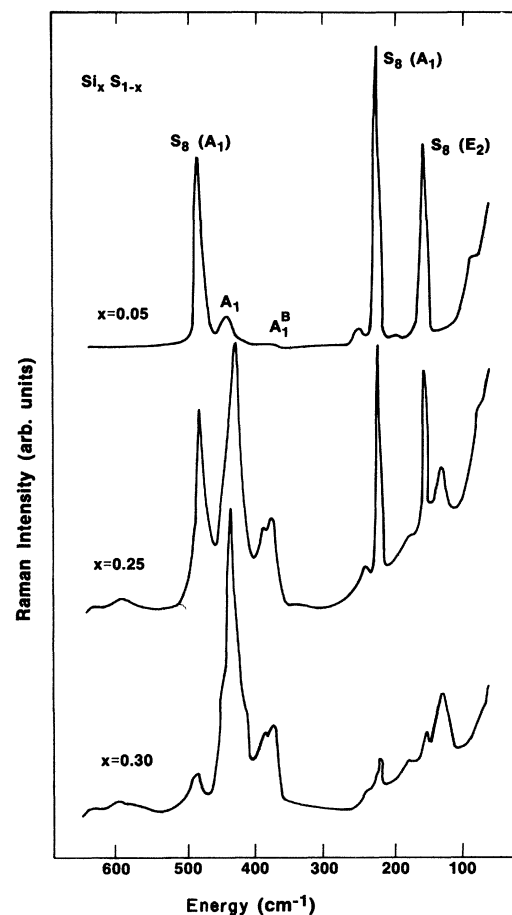

FIG. 1. Raman spectra of Si-poor Si_xS_{1-x} glasses. See Table I and the text (Sec. III C) for the identifications of the lines.

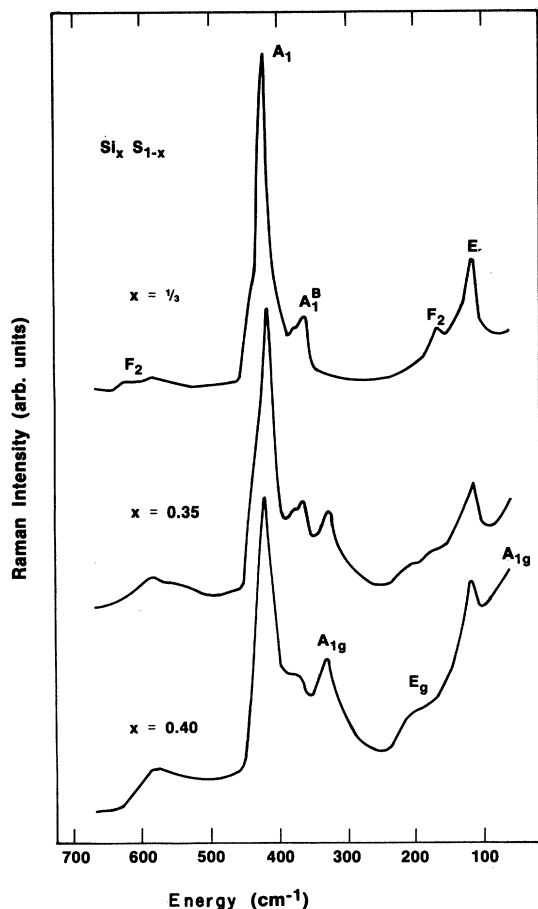FIG. 2. Raman spectra of Si-rich Si$_x$S$_{1-x}$ glasses. See Tables I and II for the identifications of the lines.

A. Glassy SiS$_2$

The spectrum of glassy SiS$_2$ is illustrated in detail in Fig. 3. Five relatively sharp spectral features (labeled E, F_2, A_1^B, A_1, and F_2) can be clearly discerned. References 1 and 2 have discussed the microscopic origins of these
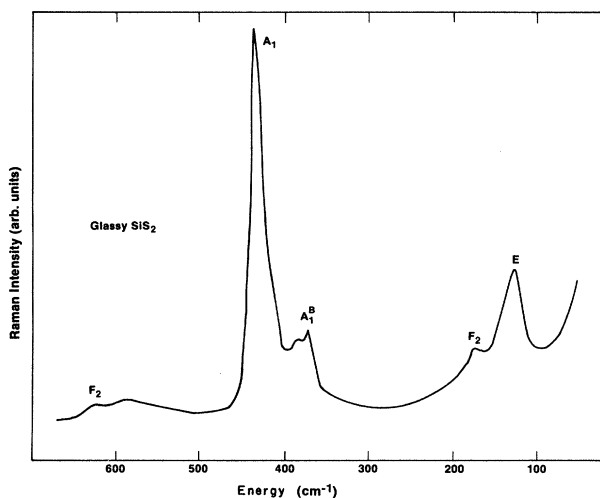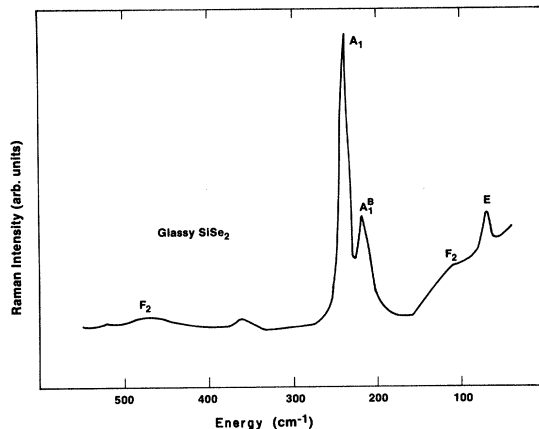

FIG. 3. Raman spectrum of glassy SiS$_2$.

FIG. 4. Raman spectrum of glassy SiSe$_2$ from Ref. 2.

Raman modes. By comparison with the experimentally observed modes of SiCl$_4$ and through the use of molecular-cluster calculations,[4] the E, F_2, A_1, and F_2 modes have been identified as the vibrational modes of Si(Si$_{1/2}$)$_4$ tetrahedral units. This analysis, along with the results of polarization measurements, is illustrated in Table I. The striking result of Ref. 1 was the realization that the mode labeled A_1^B is not a normal mode of a Si(S$_{1/2}$)$_4$ unit. As discussed in detail in Ref. 2, the microscopic origin of the A_1^B mode is a symmetric vibration of the chalcogen atoms of a bitetrahedral Si$_2$(S$_{1/2}$)$_8$ unit. The A_1^B mode is a direct indication of the existence of chainlike units in glassy SiS$_2$, and of course, medium-range atomic order. The work of Ref. 1 established that the structure of glassy SiS$_2$ is composed of randomly oriented edge-sharing SiS$_2$ tetrahedral chains. For comparison, the Raman spectrum of glassy SiSe$_2$ is shown in Fig. 4. Note that the A_1^B line in glassy SiSe$_2$ is not split; while a clear splitting is evident in the region labeled A_1^B in the glassy SiS$_2$ spectrum (Fig. 3). The origin of this difference between the spectra of glassy SiS$_2$ and SiSe$_2$ is unknown. The corresponding lines in crystalline SiS$_2$ and SiSe$_2$ are not split.[1]

B. Si-rich ($x > \frac{1}{3}$) glasses

Figure 2 shows the Raman spectra of the Si-rich glasses of this study. In addition to the five Raman modes of the SiS$_2$ clusters, three other lines appear as the Si content is increased. In the Si$_x$ Se$_{1-x}$ glass system, the first Si-rich unit to appear beyond SiSe$_2$ is the ethanelike unit Se$_3$-Si-Si-Se$_3$.[2] As in the Si-Se system, the Si-rich unit of the Si-S glasses can be identified by a comparison with the corresponding Si-halogen compound (Cl$_3$-Si-Si-Cl$_3$). The Raman mode frequencies and polarizations are compared in Table II. The good agreement found in Table II reinforces the identification of the Si-rich unit as the ethanelike S$_3$-Si-Si-S$_3$ cluster. In the Si$_x$Se$_{1-x}$ glassy system, homogeneous glasses can be prepared for $x < 0.38$.[2] The failure to form homogeneous glasses beyond $x = 0.38$ was related to the difficulty in stabilizing divalent Si compounds. Apparently, it is more difficult to stabilize the Si-S ethanelike units, since the glasses of this study become inhomogeneous beyond $x = 0.35$. In contrast to the

TABLE I. Raman modes of crystalline and glassy SiS_2 and a comparison with $SiCl_4$ and the results of a molecular-cluster calculation [polarized (P) and unpolarized (U) measurements are shown].

Mode	c-SiS_2 (cm^{-1})	a-SiS_2 (cm^{-1})	Molecular cluster [$Si(S_{1/2})_4$] (cm^{-1})	$SiCl_4$ (cm^{-1})
E	138	121(U)	121(U)	150(U)
F_2	175 181	174(U)	142(U)	221(U)
A_1^B	351	367 381(P)		
A_1	430	427(P)	380(P)	423(P)
F_2	625	625(U)	547(U)	608(U)

behavior of the Si glasses, homogeneous glasses in the Ge_xS_{1-x} and Ge_xSe_{1-x} systems can be prepared without difficulty for $x < 0.40$. In Ref. 2, the different behavior of the Si- and Ge-based glasses was attributed to the greater stability of the divalent state of Ge compared to Si. Therefore, for homogeneous Si-rich glasses, the microstructure consists of both ethanelike $Si_2(S_{1/2})_6$ and bitetrahedral $Si_2(S_{1/2})_8$ units.

C. Si-poor ($x < \frac{1}{3}$) glasses

The Raman spectra of some of the Si-poor glasses of this study are shown in Fig. 1. For very low Si concentrations (e.g., $x = 0.05$), three sharp lines are observed in addition to the lines of the SiS_2 units. These same spectral features have been observed in Ge-poor Ge-S glasses,[5] and occur near the observed Raman modes of an S_8 molecule. In the glassy Ge-S system, it was concluded that the dominant molecular species in Ge-poor glasses are $Ge(S_{1/2})_4$ tetrahedral units and S_8 ring units. As the Ge content of the glasses increases towards $x = \frac{1}{3}$, S atoms begin to link the $Ge(S_{1/2})_4$ tetrahedra. A similar description appears to hold for the Si_xS_{1-x} glasses.

A particularly significant result of the Raman studies of the Si-poor glasses is the behavior of the relative intensity of the A_1^B and A_1 lines with Si content. From the above discussion, it is clear that the A_1 line is a measure of the number of Si atoms in $Si(S_{1/2})_4$ tetrahedral units, while the A_1^B line is related to the number of Si atoms in SiS_2 chains. Figure 5 shows the fraction of Si atoms in SiS_2 chains compared to the number of Si atoms in the $Si(S_{1/2})_4$ tetrahedral units. These values have been corrected by the assumption that all of the Si atoms [or equivalently all of the $Si(S_{1/2})_4$ tetrahedral units] have entered into the SiS_2 chains at $x = \frac{1}{3}$.

The behavior of the fraction of Si atoms in SiS_2 chains

TABLE II. Indentifications of the Raman-active modes of Si_2S_6 and Si_2Cl_6 [polarized (P) and unpolarized (U) measurements are shown].

Mode	S_3-Si-Si-S_3	Cl_3-Si-Si-Cl_3[a]
$\nu_1(A_{1g})$; $\nu(XY_3)$	335(P)	351(P)
$\nu_{11}(E_g)$; $\nu(XY_3)$	205(U)	211(U)
$\nu_2(A_{1g})$; $\nu(XY_3)$		127(P)

[a]Three of the most intense Raman modes.

with Si content (x) is especially interesting. Beyond a critical Si content ($x > 0.25$), all of the Si atoms enter into the chains. For the glasses with lower Si content, some of the Si atoms evidently exist in the glassy network as isolated $Si(S_{1/2})_4$ tetrahedral units. A nearly linear decrease in the fraction of Si atoms in the chainlike units is observed with decreasing Si content. At very low Si compositions, presumably all of the Si atoms can be incorporated in the network as isolated tetrahedral units. In the Ge_xSe_{1-x} glassy system, an anomalous Raman line (the so-called A_1-companion line) is present, which has an X^5 dependence on composition.[6] Considerable controversy remains concerning the microscopic origin of the A_1-companion line and the extent of medium-range order in $GeSe_2$. Recent work suggests that the presence of small rings of atoms can account for the behavior of the A_1-companion line.[7-9] An alternate explanation for the behavior of the A_1 line involves the growth of two-dimensional $GeSe_2$ clusters.[10] This situation is potentially simpler than that of the Ge-Se system, due to the fact that the microscopic nature of the SiS_2 cluster is known and that a means of quantifying it (the A_1^B Raman line) is available. Combined Raman and infrared measurements are planned to determine the relative amounts of the $Si(S_{1/2})_4$ tetrahedral units, $Si_2(S_{1/2})_8$ bitetrahedral units, S_8 units, and fragments of S units such as bridging S
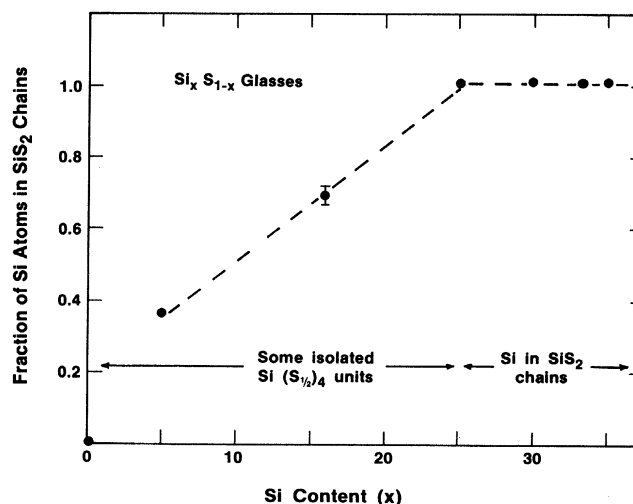

FIG. 5. The fraction of Si atoms in SiS_2 chains as a function of Si content (x). The dotted line through the experimental points is set as a guide for the eye.

atoms as a function of Si content. In addition to this, one would like to know the physical extent of the chainlike SiS_2 units in the glasses. Experimentally, this is a very difficult quantity to measure and the possibility exists that it might vary with composition. Computer-generated models in which the results of the combined Raman and infrared measurements are treated as inputs might be able to deduce the average SiS_2 chainlike cluster lengths.

A final note concerns the relative intensity of the split feature in glassy SiS_2, identified as A_1^B modes. Both the splitting and the relative intensity of these two lines are independent of composition. This shows that they are associated with the same cluster in the glasses.

IV. CONCLUSIONS

Raman studies of Si_xS_{1-x} glasses have provided a relatively detailed description of the atomic structure of these materials. At $x = \frac{1}{3}$, the glass is composed of randomly oriented chains of edge-sharing $Si(S_{1/2})_4$ tetrahedra. In Si-rich glasses $(x > \frac{1}{3})$, the excess Si is accommodated in

the glassy structure as ethanelike S_3-Si-Si-S_3 units. The structure of the Si-poor glasses $(x < \frac{1}{3})$ is considerably more complex. Starting from pure amorphous S which consists primarily of S_8 molecular units, the addition of small amounts of Si leads to the formation of isolated $Si(S_{1/2})_4$ tetrahedral units in a matrix of S_8 rings. Further additions of Si result in a growth of edge-sharing SiS_2 tetrahedral chains in the glass. From $x = 0.05$ to $x = 0.25$, a nearly linear increase in the fraction of Si atoms in the SiS_2 chains is observed with composition. In this same region of composition, S atoms begin to adopt a role in linking the $Si(S_{1/2})_4$ tetrahedra together. Beyond $x = 0.25$, all of the Si atoms in the Si-poor glasses enter into the edge-sharing SiS_2 units.

ACKNOWLEDGMENTS

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