

Possible Role of Concentration Fluctuations and Excess Volume in the Photodissolution of Metals in As-S Glasses

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Regarding the composition dependence of photodoping rate of Ag in As_xS_{1-x} glasses, many authors have noted a maximum in the composition range $0.2 < x < 0.4$. In the present paper, the origin of such composition dependence has been investigated by using two different approaches. In the first approach, the possibility to relate the concentration fluctuation of the host glass to the photodoping rate has been studied. In the second approach, the composition dependence of the photodoping rate has been compared with the excess volume. Although not conclusive, the result of the second approach pointed out a possible correlation.

§1. Introduction

Glassy chalcogenide semiconductors show a wide variety of light induced phenomena such as photodarkening, photobleaching, photo-polymerization, photodoping, etc.¹⁻⁴⁾ In the photodoping phenomenon, illumination induces the dissolution of metals such as Ag into glassy chalcogenide semiconductors. Despite the extensive studies¹⁻⁵⁾ performed after its discovery,⁶⁾ theory concerning the microscopic mechanism of photodoping has not yet received general acceptance.

Regarding the composition dependence of photodoping rate of Ag in As_xS_{1-x} glasses, many authors have noted a maximum in the composition range $0.2 < x < 0.4$.⁷⁻¹⁰⁾ In previous studies, such a composition dependence have been discussed in the light of thermodynamic model proposed by Owen et al.¹¹⁾ Although the application of thermodynamic concepts to non-equilibrium glassy systems remains as a fundamental problem, the approaches seem very successful. Concerning this point, it is argued that the free energy can be defined within the experimental timescale.¹²⁾ The thermodynamic approach has been used also to explain the composition dependence of photoinduced surface deposition.¹³⁾

In the present paper, the origin of the composition dependence of photodoping rate is investigated by using two different approaches. The first one is based on the theory of concentration fluctuations and the second one is based on the concept of excess volume.

§2. Concentration fluctuations and the photodoping rate

Following the theory of liquids, the concentration fluctuation for a two component system is given by¹⁴⁾

$$S_{cc}(0) = \frac{c(1-c)}{1+c(1-c)f(c)}, \quad (2.1)$$

$$f(c) = \delta^2 \left[1 - \frac{2\beta\delta w}{(\beta - 1)^3 k_B T} \right], \quad (2.2)$$

$$\delta = \frac{V_1 - V_2}{cV_1 + (1 - c)V_2} = \frac{N}{V}(V_1 - V_2), \quad (2.3)$$

$$\beta = \frac{V_1}{V_2}, \quad \beta < 1 \quad (2.4)$$

where $S_{cc}(0)$ is the long wavelength limit of the concentration-concentration structure factor introduced by Bhatia and Thornton,¹⁵⁾ c and $(1 - c)$ are the concentrations of component 1 and 2, respectively, V_1 and V_2 are the molar volumes, w is the interchange energy which gives a measure of the ordering potential, and the other symbols have the usual meaning. Eqs. (2.1)–(2.4) have been used frequently to study the thermodynamic properties of liquid alloys.^{14,16)} Since the second concentration derivative of the Gibbs free energy is related to $S_{cc}(0)$ by

$$S_{cc}(0) = \frac{k_B T}{(\partial^2 G / \partial c^2)_{P,T,N}}, \quad (2.5)$$

the quantity $S_{cc}(0)$ contains information about the stability of the system. Then, the following question arises. Is not the photodissolution of metals related to the concentration fluctuations of the host glass?

In order to investigate this possibility, a preliminary result on the composition dependence of $S_{cc}(0)$ is given below. In the following, it is assumed that the structure of the liquid remains unchanged through the glass transition. The behavior of Eqs. (2.1)–(2.4) is illustrated in Fig. 1 by curves A, B, and C. The curve A corresponds to the case of ideal mixture. The curves A, B and C have been calculated by assuming that the dilatation factor δ , the molar volume ratio β and the interchange energy w remain constant with the variation of composition. We can see that, nothing of special occurs in the behavior of $S_{cc}(0)$ which can be related to the composition dependence of photodoping rate (see Fig. 4). In order to put the expression of $S_{cc}(0)$ more close to a real system, the dilatation factor is generalized as

$$\delta(c) = \frac{1}{V(c)} \left[\frac{\partial V(c)}{\partial c} \right]_{P,T,N}, \quad (2.6)$$

where $V(c)$ is the molar volume of the system when the concentration of the component 1 is c . Eq. (2.6) reduces to Eq. (2.3) when the molar volume of a two component system varies linearly with concentration c .

Analogously to Eq. (2.6), formally it is possible to write a generalized expression for the molar volume ratio $\beta(c)$ and the interchange energy $w(c)$. However, in the present study, the composition dependence of these quantities are ignored, because the experimental data to evaluate $\beta(c)$ and $w(c)$ are not available.

Figure 2 shows the concentration dependence of the molar volume for the glassy system As_xS_{1-x} obtained from the density data reported by Nemilov.¹⁷⁾ The density

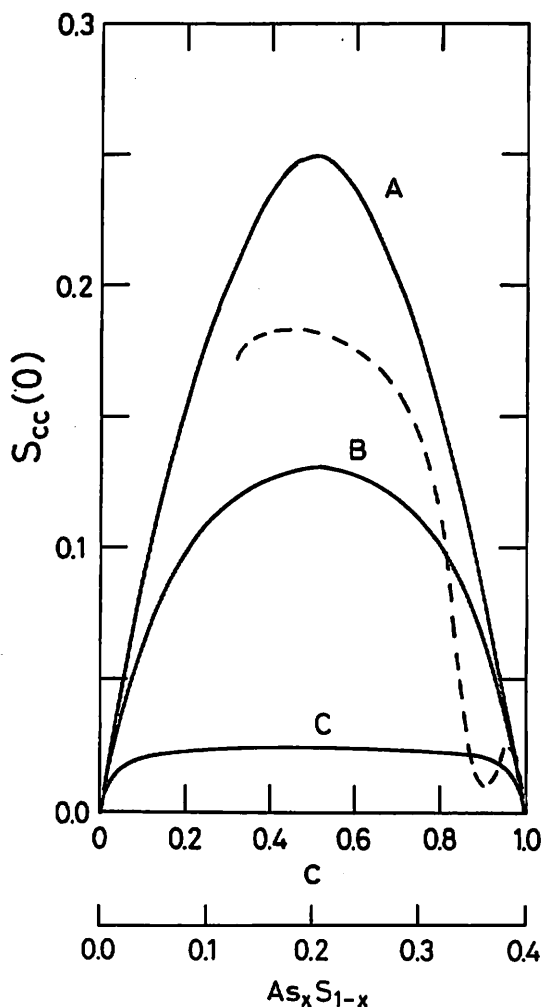


Fig. 1. Concentration fluctuations $S_{cc}(0)$ as a function of concentration c . The curves A, B and C show the behavior of Eqs. (2.1)–(2.4) with the following values of the parameters. Curve A [$\beta = 1, \delta = 0, w/k_B T = 0$]; curve B [$\beta = 0.93, \delta = -0.2, w/k_B T = -0.1$]; curve C [$\beta = 0.93, \delta = -0.2, w/k_B T = -1.0$]. The broken curve has been calculated by using $\beta = 0.93, w/k_B T = -1.0$ and by replacing Eq. (2.3) to Eq. (2.6). The scale outside the figure is for a pseudobinary system $(As_2S_3)_c S_{1-c}$.

data are not available for the entire range of composition, because the glass forming region in this system is limited in the range $0.05 < x < 0.45$.¹⁰⁾ Therefore, in the analysis presented in this section, the system $As_x S_{1-x}$ is considered as a pseudobinary system composed of As_2S_3 and S, i.e. $(As_2S_3)_c S_{1-c}$.

The molar volume of the system at the composition As_2S_3 is $15.41 \text{ cm}^3/\text{mol}$. If we extrapolate the data to $x = 0$ by a broken straight line as shown in Fig. 2, the

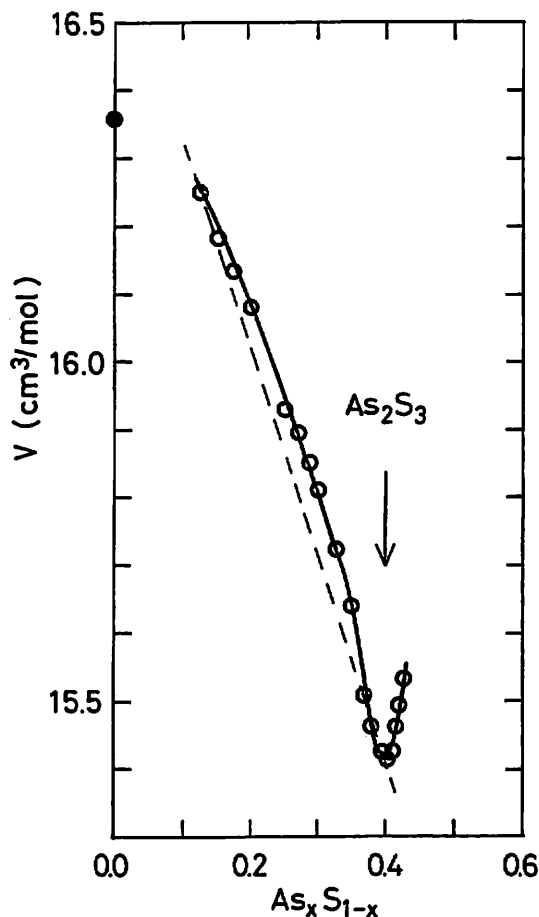


Fig. 2. Composition dependence of the molar volume for the glassy system As_xS_{1-x} obtained from the density data. [Ref. 17 (o) and ref. 18 (•)]. For the meaning of the broken straight line see the text.

molar volume of S is estimated to be $16.64 \text{ cm}^3/\text{mol}$. The ratio between these two quantities gives the value of the parameter β used in the calculation of curves B and C shown in Fig. 1. In Fig. 2, the molar volume of S reported by another group¹⁸⁾ is also shown for comparison (closed circle).

The dilatation factor evaluated by using the molar volume data of Fig. 2 is shown in Fig. 3. In the figure we observe a large negative peak in the composition range $0.3 < x < 0.4$. However, since the dilatation factor is a very sensitive quantity, it contains a large uncertainty. So, we must be careful in the interpretation of this peak. The broken line shown in Fig. 3 illustrates the behavior of Eq. (2.3). The curves B and C shown in Fig. 1 have been calculated by using the value of $\delta = -0.2$, that corresponds to the broken line in Fig. 3.

The behavior of $S_{cc}(0)$ calculated by using the composition dependent dilatation factor is shown by the broken curve in Fig. 1. We can see that the curve follows the

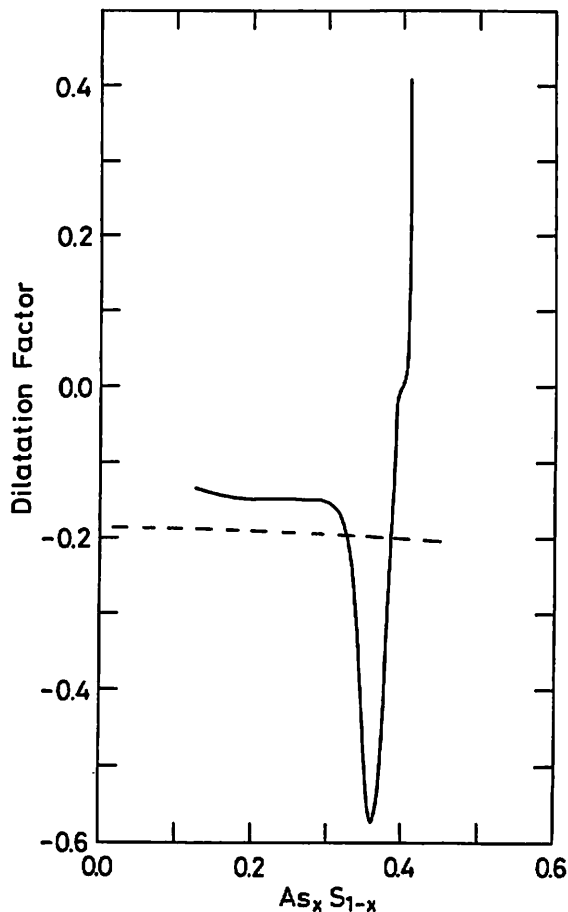


Fig. 3. Dilatation factor obtained from the molar volume. The broken line shows the behavior of Eq. (2.3).

behavior of curves A – C. The deviation observed in the range $0.8 < c < 1.0$ must not be taken so seriously, because it arises from the large negative peak of Fig. 3 which contains a large uncertainty.

As a conclusion of this section we can say that, from the behavior of concentration fluctuation obtained in the present study, we can not extract a definite conclusion concerning the composition dependence of photodoping rate in glassy As_xS_{1-x} . The composition dependence of the photodoping rate found experimentally is shown in Fig. 4.

§3. Excess volume and the photodoping rate

By looking at Fig. 2, we observe that the molar volume in the composition range of $0.1 < x < 0.4$ is convex upward. It will be interesting to see if this behavior

is or not related with the composition dependence of photodoping rate. By taking the broken straight line as a reference volume, the normalized excess volume has been plotted as a function of composition as shown by the curve denoted EV in Fig. 4. The composition dependence of the photodoping rate reported by two groups (denoted by PD) are also shown in the same figure. We can see that the excess volume correlates relatively well with the photodoping rate, specially in the peak position. However it is obvious that the determined excess volume depends on the reference volume. For instance, if we draw a straight line between the molar volumes of As_2S_3 and S denoted by a full circle, a different result is obtained. In the present study, the broken straight line has been adopted, because in the data collection¹⁹⁾ the molar volume of $\text{As}_x\text{S}_{1-x}$ seems to vary linearly in the range $0 < x < 0.25$.

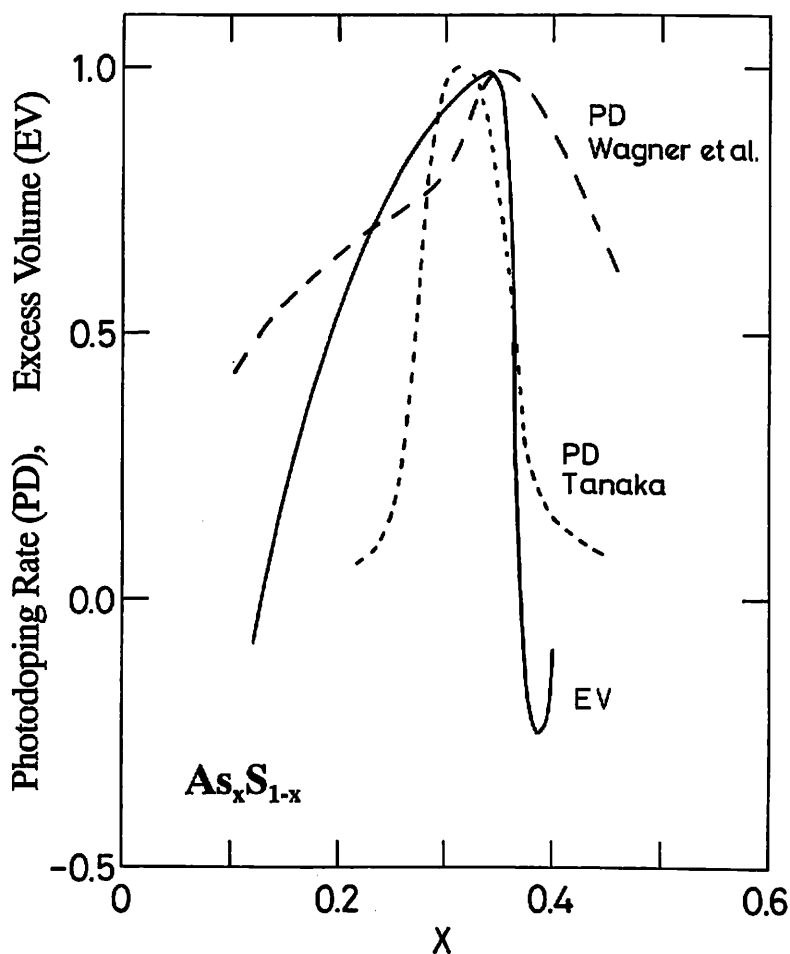


Fig. 4. The composition dependence of photodoping rate of Ag in $\text{As}_x\text{S}_{1-x}$ reported by Wágner et al.⁹⁾ and Tanaka¹⁰⁾ are compared with the excess volume extracted from the molar volume data. Both quantities are normalized at their maximum values.

§4. Conclusion

In the present paper, the origin of the composition dependence of photodoping rate, has been investigated by using two different approaches. In the first approach, the possibility to relate the concentration fluctuation of the host glass to the photodoping rate has been studied. The calculated long wavelength limit of the concentration-concentration structure factor does not show any characteristic feature that can be related to the composition dependence of the photodoping rate. In the second approach, the composition dependence of the photodoping rate has been related to the excess volume. Although not conclusive, the result of the second approach pointed out a possible correlation.

The study presented in this paper is very crude. So, the results obtained in this paper must be understood as preliminary. Since the working hypotheses adopted in the present paper are physically sound, further detailed studies along this line are necessary in order to clarify the origin of the composition dependence of the photodoping rate.

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