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In-situ Observation on Growth of Crystals out of Glass Surface Caused by Electron Beam Bombardment

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Needle-like crystals grew in the dendritic form out of the surface of a tiny fragment of fresh glass when it was bombarded with intense electron beams in an electron microscope. Factors controlling this phenomenon were examined qualitatively. The phenomenon seemed to be limited to glasses containing mobile atoms such as Na and Pb, to fresh samples not contacted with water and other contaminants and to the part of the glass sample where carbon film was lacking. Besides the crystal growth, the electron bombardment caused the formation of bubbles in the glass samples. Both the phenomena were given a tentative interpretation based on the theory given by Lineweaver, which assumes displacement of alkali ions due to impregnated electrons in alkali-containing glass.

I. INTRODUCTION

In the course of electron microscopic observation of phase separation of glass, a peculiar phenomenon of crystal growth was noticed to occur. It was observed in the electron microscope that needle-like crystals grew outwards at the surface of glass when the glass was bombarded by intense electron beams. In the present paper the result of systematic observation of this phenomenon is presented. Apparent bubble formation within glass which is caused by electron bombardment is also described.

II. EXPERIMENTAL PROCEDURE

1. Sample preparation

A commercial silica glass and three silicate glasses prepared from reagent grade chemicals (Table 1), were used for the observation in an electron microscope.

Glasses were fractured by hammering strongly to obtain fine fragments having a thickness less than 500 Å which allows direct transmission observation in the electron microscope. A pertinent portion of the fragment were placed on an acetyl cellulose film and covered with a carbon film. They were bonded onto a copper grid with epoxy resin. The arrangement of a glass fragment on the copper grid is shown schematically in Fig. 1. After mounting the sample, one of the following treatments regarding the carbon film was applied to the sample.

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Table 1. Compositions and Melting Condition of Glasses Used

Symbol	Composition (Mole %)				Melting condition	
	SiO_2	Li_2O	Na_2O	PbO	Temperature	Time
SiO_2	100	—	—	—	—	—
L3S	75	25	—	—	1400°C	2 hr
N3S	75	—	25	—	1450°C	2 hr
Pl. 5S	60	—	—	40	1100°C	1 hr

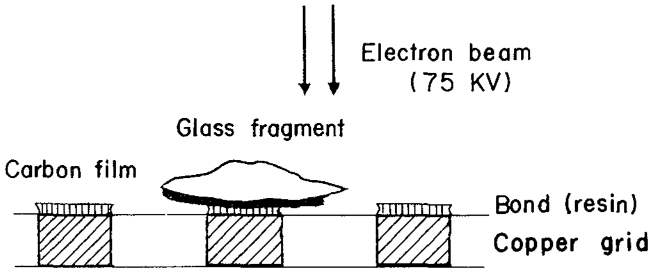


Fig. 1. Schematic view of the arrangement of a glass sample in the electron microscope.

(a) Carbon film was peeled off with a pointed tweezer under an optical microscope only at the part of a fragment that was expected to be observed in the electron microscope—no carbon film.

(b) Very thin carbon film was deposited on the surface of the fragment where no carbon was deposited before—thin carbon film.

(c) Thick carbon film was deposited—thick carbon film.

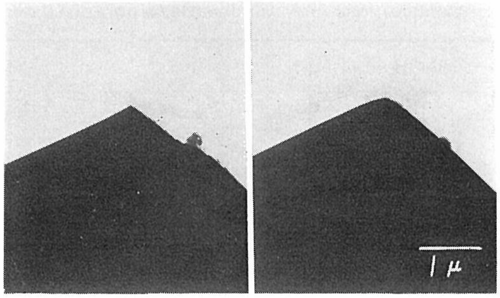
2. Electron microscopic observation

A Hitachi electron microscope model HU-11 D was used. The acceleration voltage and the filament current were kept at 75 kV and 40 μA, respectively. In order to have a high electron beam density on the sample surface, the beam was focused to a diameter less than 5 μ with the aperture condenser. Upon electron microscopic observation the trap equipped in the sample chamber was filled with liquid nitrogen to reduce contamination of the glass fragment.

III. RESULTS AND DISCUSSION

1. Growth of crystals on fragments having no carbon film

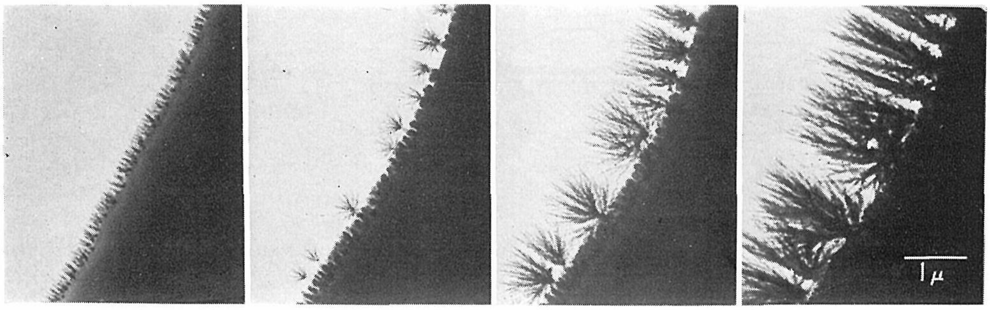
Representative electron micrographs exhibiting the effect of electron bombardment on the fragments with a portion of carbon film taken away are shown in Figs. 2, 3, 4, and 5, respectively, for the SiO_2, $Li_2O{\cdot}3SiO_2$, $Na_2O{\cdot}3SiO_2$, and $PbO{\cdot}1.5SiO_2$ glasses. Almost no change was induced in SiO_2 glass (Fig. 2), while needle-like growth of some



Irradiation 0 min. 30 min.

Glass; SiO_2 (corner)
Carbon film; None
Electron beam; Strong (small focus)

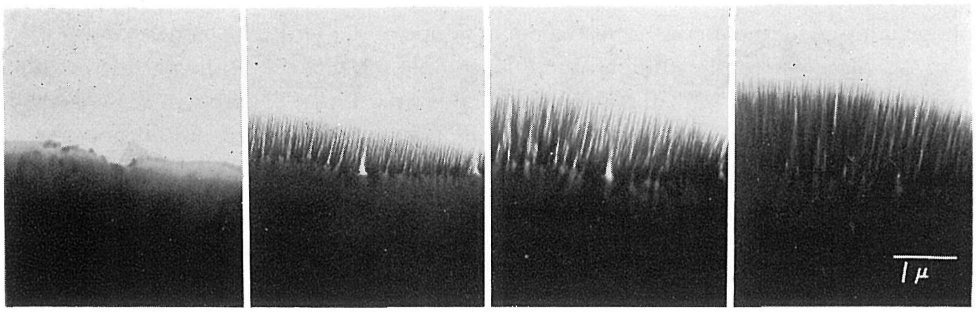
Fig. 2. Electron bombardment of the SiO_2 glass.



Irradiation 1 min. 5 min. 15 min. 30 min.

Glass; $Li_2O \cdot 3SiO_2$
Carbon film; None
Electron beam; Strong (small focus)

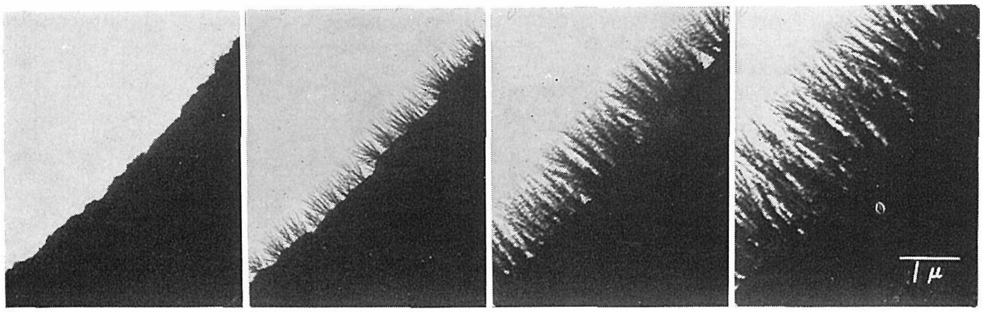
Fig. 3. Crystal growth on the surface of the $Li_2O \cdot 3SiO_2$ glass.



Irradiation 0 min. 5 min. 15 min. 30 min.

Glass; $Na_2O \cdot 3SiO_2$
Carbon film; None
Electron beam; Strong (small focus)

Fig. 4. Crystal growth on the surface of the $Na_2O \cdot 3SiO_2$ glass.



Irradiation 0 min. 5 min. 15 min. 30 min.

Glass; $PbO \cdot 1.5SiO_2$
Carbon film; None
Electron beam; Strong (small focus)

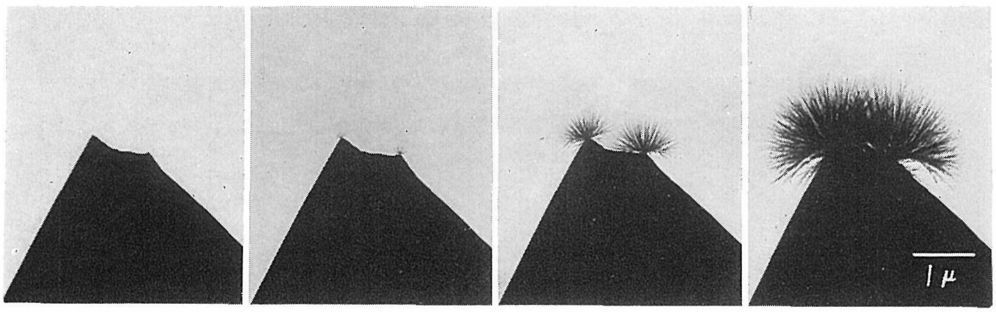
Fig. 5. Crystal growth on the surface of the $PbO \cdot 1.5SiO_2$ glass.

substance occurred outward from the surface of the fragments in other glasses (Figs. 3, 4, and 5). The direction of growth was approximately rectangular to the surface.

It is seen that the needles grow uniformly, that is, throughout the irradiated surface, in Figs. 4 and 5, whereas they grow less uniformly in Fig. 3. A large number of observations indicated that this difference is not due to the composition of the glass but due to different degree of contamination of the sample taking place before the electron beam bombardment; heavier contamination of the sample caused the number of needles to be smaller, as shown in Fig. 3.

The average growth rate of the needle-like crystals was about 10 Å/sec for the alkali silicate glasses $Li_2O \cdot 3SiO_2$ and $Na_2O \cdot 3SiO_2$ and about 12 Å/sec for the lead silicate glass $PbO \cdot 1.5SiO_2$, under the conditions of the present experiment.

Figure 6 shows the growth of crystals on a fragment of the glass $PbO \cdot 1.5SiO_2$ which has two pointed corners. The growth of crystals took place only at the pointed corners



Irradiation 0 min. 5 min. 15 min. 30 min.

Glass; $PbO \cdot 1.5SiO_2$ (corner)
Carbon film; None
Electron beam; Strong (small focus)

Fig. 6. Crystal growth at pointed corners of the glass fragment.

in contrast with the fragments which have no pointed corner. The similar crystal growth was observed also for $Li_2O{\cdot}3SiO_2$ and $Na_2O{\cdot}3SiO_2$ glasses.

Observations during growth of the needle-like crystals indicated that the needles grown from a spot of the fragment surface did not contact with each other at their tips; when a needle happened to grow toward another needle that was growing from the other spot and the two were about to contact with each other, a repulsion force seemed to act between the two, and one of the needles broke away by a shock. This observation indicates the presence of electric charges with the same sign on the needle-like crystals.

2. Identification of crystals

An attempt was made to identify the needle-like crystals using the method of limited field electron diffraction. Diffraction patterns consisted of three diffuse haloes for all the glasses as shown in Fig. 7. Considering that (1) crystal growth is not seen for non-alkali SiO_2 glass and (2) the d spacings calculated based on the three haloes for the $Li_2O{\cdot}3SiO_2$ glass are different from those for the $Na_2O{\cdot}3SiO_2$ glass, the needle-like crystals may consist of an element or a compound involving a corresponding alkali element. From the comparison of d spacings calculated from the haloes with those in the literature obtained from the x-ray structural analysis, the present authors tend to identify the compounds as alkali oxides tentatively. A definite conclusion will be postponed, however, until further experimental development for obtaining clearer diffraction patterns.

3. Electron bombardment of fragments with carbon film

Figure 8 shows the effect of electron bombardment on a fragment of the $Na_2O{\cdot}3SiO_2$ glass having a pointed corner and covered with a thin carbon film. At the initial stage of bombardment, the fragment deformed under electron beams and at the later stage needle-like crystals started to appear at the pointed corner and continued to grow. In the present condition of electron bombardment the time necessary for the start of crystal growth was about 12 minutes. This time period varied from a fragment to another probably because many shape factors such as the thickness, size and shape of

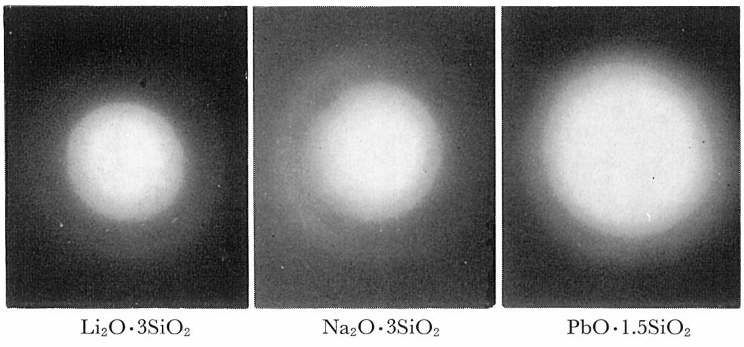
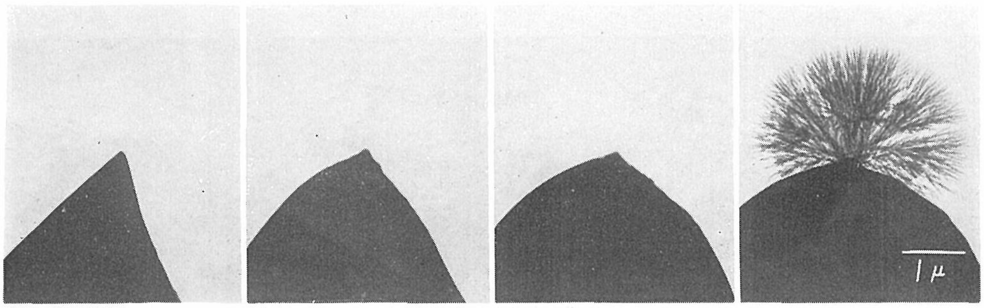


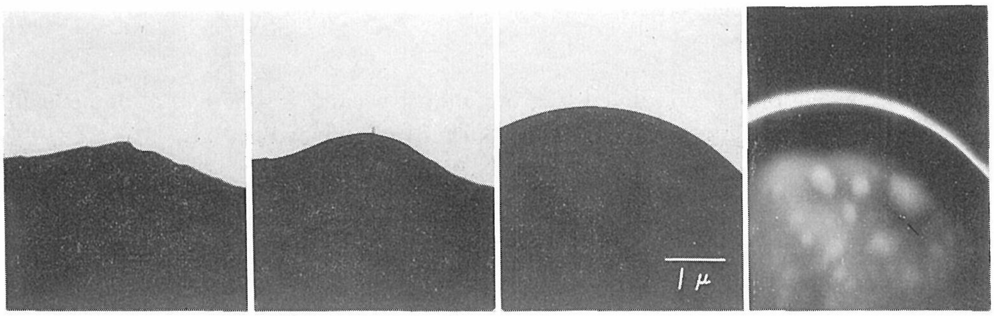
Fig. 7. Electron diffraction patterns of crystals formed on glass fragments irradiated with strong electron beams.



Irradiation 0 min. 5 min. 10 min. 30 min.

Glass; $Na_2O \cdot 3SiO_2$
Carbon film; Thin
Electron beam; Strong (small focus)

Fig. 8. Deformation and crystal growth under electron beams.



Irradiation 0 min. 5 min. 20 min. 31 min.

(Dark ground)

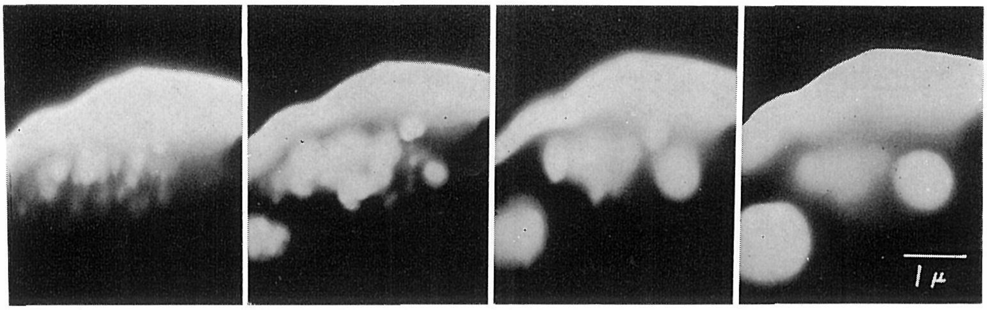
Glass; $Na_2O \cdot 3SiO_2$
Carbon film; Thick
Electron beam; Strong (small focus)

Fig. 9. Deformation and bubble formation by electron bombardment.

the pointed corner affected it. The similar deformation and crystal growth were observed also for the $Li_2O \cdot 3SiO_2$ and $PbO \cdot 1.5SiO_2$ glasses.

When the carbon film was thicker, only the deformation of the sample was observed and no crystal growth took place, until after 60 minutes' bombardment, as shown in Fig. 8 for the $Na_2O \cdot 3SiO_2$ glass. It was found by the observation of the dark image after 31 minutes' irradiation that there appeared a portion of the fragment where electron beams easily penetrated, as shown by the 4th photograph of Fig. 9. This portion may represent presence of a void, or a bubble, within glass.

To investigate this phenomenon in more detail the glass fragment with thick carbon film was bombarded with very intense electron beams provided by removing the aperture condenser. The dark image microphotographs are shown in Fig. 10. Occurrence of bubbles and, at the same time, deformation of the fragments started after 5 minutes'



Irradiation 5 min. 15 min. 30 min. 60 min.

(Dark ground)

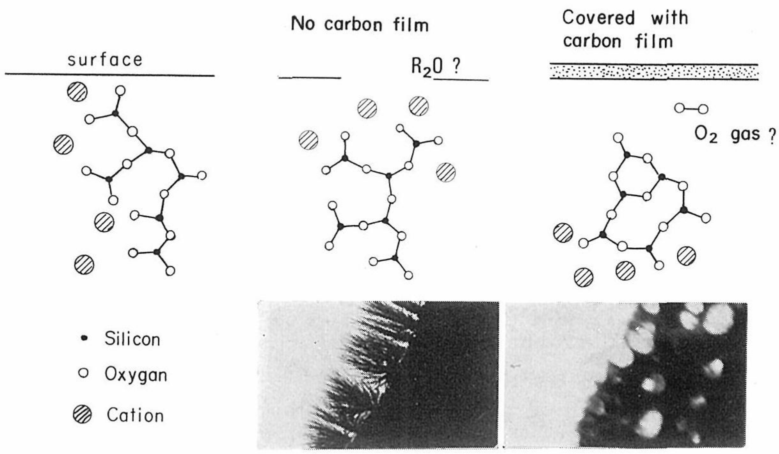
Glass; $Na_2O \cdot 3SiO_2$
Carbon film; Thick
Electron beam; Very strong (no condenser aperture)

Fig. 10. Bubble formation in a glass fragment by electron bombardment.

irradiation. The bubble continued to grow until it became a sphere of a diameter in the order of magnitude of 1 μ after 60 minutes' irradiation.

4. Mechanism of crystal growth and bubble formation

Crystal growth and bubble formation caused by electron bombardment can be explained on the basis of the theory suggested by Lineweaver.[1] Figure 11 shows the changes occurring in the glass network schematically. The high energy electrons, entering the glass, come to rest at some depth within the glass after dissipation of their energy, producing a net negative charge. Then positive sodium ions move towards

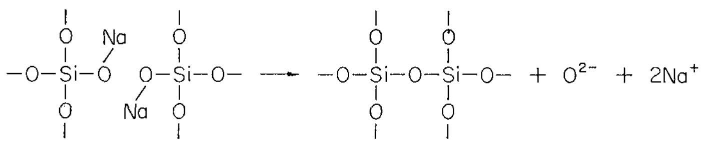


Before irradiation After irradiation

Fig. 11. Schematic representation illustrating the movement of cation leading to the crystal growth and bubble formation.

the negative charge region and become neutralized. At a region where there is no conductive carbon coating, a negative charge region which turns to a sodium rich region would be formed at near surface, as shown in Fig. 11. It is quite probable that the sodium atoms form crystals because the temperature high enough for the crystal growth may be given by electron bombardment.

For the glass wholly covered with a thick, highly conductive carbon film, the electrons near the surface are carried away through the film and only those electrons that are impregnated more deeply within glass form a negative charge region which turns to a sodium rich region by attracting sodium ions from the neighboring region. It is supposed then that the region nearer to the surface contains extra oxygen ions left by the reaction,



and such oxygen ions can form O_2 gases, the electrons being carried away through the carbon film. It is believed that this is the mechanism of bubble formation observed in the present study, although the gas in the bubbles was not identified as oxygen yet. It should be noted that Dudek observed bubbles formed by electron bombardment using an optical microscope.[2]

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(1) J. L. Lineweaver, *J. Appl. Phys.*, **34** 1786 (1963).
(2) H. J. Dudek, *Glastechn. Ber.*, **41** 10 (1968).