

Structure and Optical Properties of Boron-Silicon Amorphous Films

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Interrelations between the atomic structure and optical properties of B-Si amorphous films, prepared by electron-beam deposition, were studied. Radial distribution functions were calculated by Fourier transformation of the interference functions obtained by X-ray diffraction method. Optical absorption edge spectra were measured and optical band gaps were evaluated from Tauc plot. The structure of a boron-rich amorphous phase, constructed with clusters, such as B_{12} clusters, changes to the random network structure of amorphous silicon at around 20 at%Si with increasing Si concentration. At the same time, the characteristic density of states at the band edges for amorphous semiconductors with complicated structure changes to that with rather simple structure. On the average, one of boron atoms around a silicon atom in the structure of crystalline B_5Si is replaced by one silicon atom in 16at%Si amorphous phase, which has approximately the same silicon concentration as c- B_5Si . A small new peak is observed at 0.250 nm in the radial distribution function for amorphous boron.

Keywords: boron-silicon, amorphous film, B_{12} cluster, atomic structure, optical band gap

1. INTRODUCTION

Some boron-rich solids are semiconductors composed of 12-atom clusters (B_{12} clusters). Each boron atom occupies on a vertex of an icosahedron and each B_{12} cluster has a tendency to connect to neighboring B_{12} clusters along six five-fold axes. Since the inter-cluster bond between B_{12} clusters is as strong as the intra-cluster one, addition of other atoms to the boron-rich solids causes substantial deformation of B_{12} clusters and change in the bonding nature around them. It has been reported that, at the same time, the properties of the boron-rich solids, such as energy gap, are significantly altered by this effect.¹⁾ Hence, the properties of the boron-rich solids can be considered to depend strongly on the presence of B_{12} clusters and the bonding nature around them.

Generally, an amorphous phase is advantageous in researching a change in structure and properties depending on composition, since the amorphous single phase can be formed over a wide composition range. Amorphous structure in the boron-rich solids has also been considered to be constructed of the B_{12} clusters.²⁾ Thus, the network of B_{12} clusters can change to that of sp^3 -covalent bonds in B-Si amorphous solids with increasing Si concentration. Consequently, studies on composition dependence of the structure and properties of B-Si amorphous solids are expected to demonstrate the effects of differences between bonds in B_{12} clusters and typical covalent bonding on the properties of the amorphous solids.

In the present study, we prepared B-Si amorphous films and studied the relation between structure and optical properties.

2. EXPERIMENTAL

The films were prepared by electron-beam evaporation from chunks of B (99.9 %) and Si (99.999 %). They were deposited on quartz glasses, slide glasses, and aluminum foil at a rate of 0.1-1.0 nm/sec.

The pressure during evaporation was $1-2 \times 10^{-6}$ Torr. The thickness of the films measured with a quartz oscillator was 200 nm. We obtained powder samples by dissolving the aluminum foil substrate using hydrochloric acid. The chemical compositions of the films were determined by Electron Spectroscopy for Chemical Analysis (ESCA).

X-ray diffraction patterns for the powder samples were measured to determine phases, using Cu-K α radiation. The X-ray scattering intensities from amorphous boron (a-B) powders were measured for atomic structure analysis, using Mo-K α radiation monochromated by a graphite (0002) crystal. The purity of them was 99.9 %. The sample was packed in a glass capillary with 1.98 mm in inner diameter and 10 μ m in wall thickness. Scattering intensities were measured from two of the amorphous films evaporated on the slide glass substrates at the BL-7C at the Photon Factory in Tsukuba, Japan. They were measured by the Seemann-Bohlin method with an X-ray incident angle to the sample of 0.5 degrees, using radiation with $\lambda=0.9$ Å monochromated by a Si (111) crystal. The method of analysis has been described in detail in ref. 3 and ref. 4.

Optical absorption edge spectra of the films deposited on the quartz glass substrates were measured with a spectrophotometer at a wavelength between 190-2600 nm. Detailed procedure of optical measurements has been described elsewhere.⁵⁾

3. RESULTS AND DISCUSSION

Four B-Si amorphous films (average Si concentration: 7 at%Si, 16 at%Si, 34 at%Si, and 73 at%Si), a-B film, and a-Si film were obtained. Figure 1 shows the depth profiles of Si concentrations determined by ESCA measurements. The Si concentration of the films depended more strongly on deposition rates than on the Si concentration of raw materials because B and Si are different in melting point and vapor pressure. Each film contained less than 2 at% carbon and 6 at% oxygen.

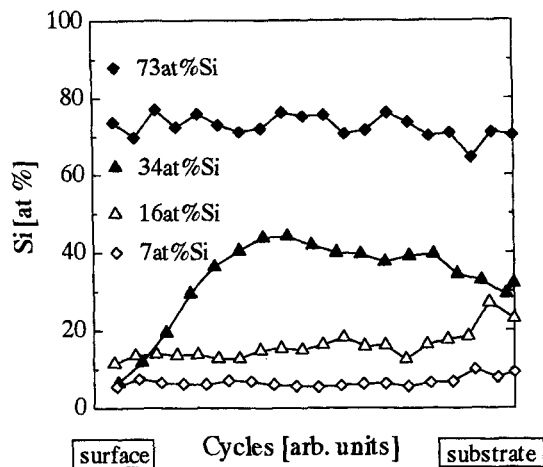


Fig. 1 Depth profiles of Si concentrations in the films determined by ESCA

Figure 2 shows the X-ray diffraction patterns of the films. The formation of amorphous phases is confirmed from appearance of halo patterns. The Bragg peaks of aluminum and silicon are observed. However, the aluminum phase was part of the substrates that were not dissolved in the hydrochloric acid and the films did not contain the aluminum phase. Since the concentration of crystalline Si was less than 1at%, we consider that the contribution of the crystalline Si phase to atomic structure and optical properties can be neglected. It is observed that the X-ray diffraction patterns of the films systematically change with increasing Si concentration and the patterns are divided into two types, namely the patterns similar to that of a-B and those similar to a-Si, between 16 at%Si and 34 at%Si. It suggests a change in atomic structure between 16 at%Si and 34 at%Si from complicated structure similar to a-B to simple structure

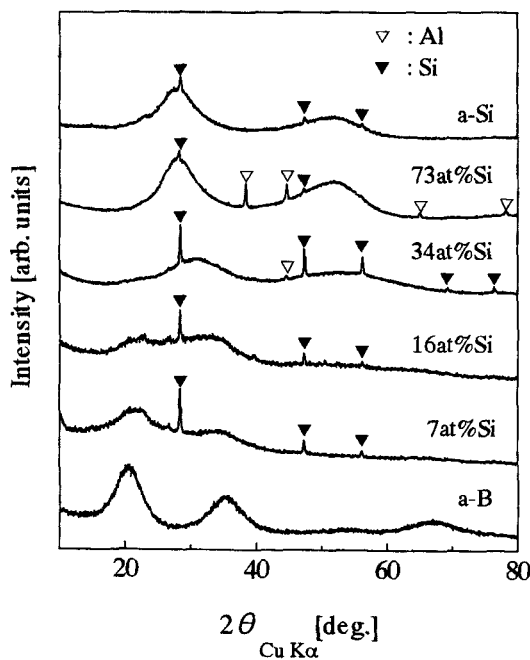


Fig. 2 X-ray diffraction patterns of the films

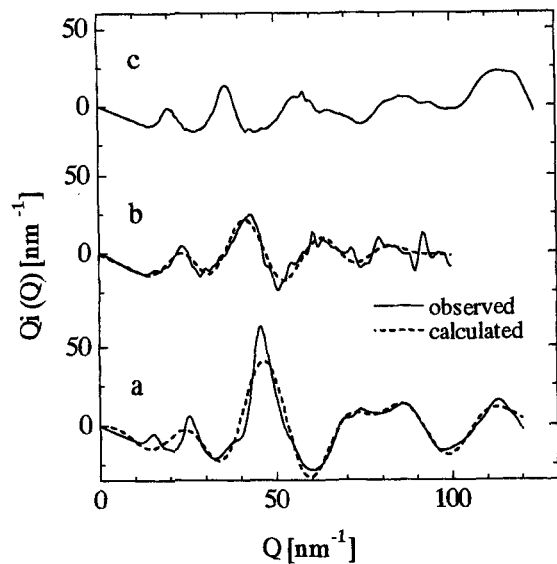


Fig. 3 Interference functions for a-B (curve a), a-16at%Si (curve b), and a-Si (curve c)

similar to a-Si.

We mention the linkages in crystalline boron. Four crystalline modifications of boron are known to exist: α -rhombohedral boron (α -rhomb-B), β -rhombohedral boron (β -rhomb-B), α -tetragonal boron, and β -tetragonal boron (tetra-B). But α -tetragonal boron has been said not to be found without the presence of foreign atoms such as carbon and nitrogen.⁹ The B_{12} clusters in α -rhomb-B are bound together along their pseudo-fivefold axes with the same orientation (in phase); whereas the B_{12} clusters in β -rhomb-B are bound along them with a rotation of $\pi/5$ with respect to each other (out of phase). Although the bonds between the B_{12} clusters in tetra-B are similar to those in β -rhomb-B, the B_{12} clusters in tetra-B are bound together along the bending pseudo-fivefold axes. We call them pseudo out of phase.

In a-B sample, 16at%Si amorphous film (a-16at%Si), and a-Si film, radial distribution functions (RDF) were able to be calculated by Fourier transformation of the interference functions obtained by X-ray diffraction method. The interference functions, $Q_i(Q)$, are shown in Fig. 3. They were truncated at a wave vector $Q = 120 \text{ nm}^{-1}$ for a-B, $Q = 100 \text{ nm}^{-1}$ for a-16at%Si, and $Q = 124 \text{ nm}^{-1}$ for a-Si, where $Q = 4\pi \sin \theta / \lambda$, 2θ is a scattering angle and λ is a wavelength.

Figure 4 shows the RDF for a-B together with the coordination numbers of β -rhomb-B and tetra-B. Table I shows the atomic distances and coordination numbers of a-B together with those of β -rhomb-B and tetra-B. The atomic distances and coordination numbers of a-B were calculated using the least-squares variational method^{4, 7} for the interference function. In this method, the structure of amorphous solids is assumed to be definite molecular structure within a critical distance, and to have no structure beyond this distance. The interference function is calculated from the model structure and compared with the observed one. The calculated

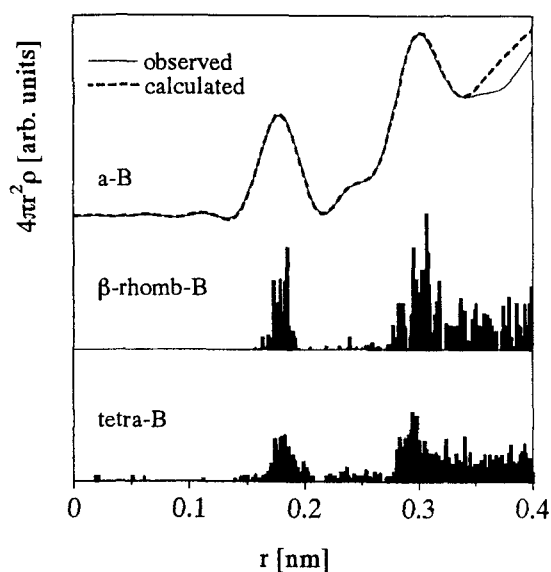


Fig. 4 Radial distribution function for a-B and coordination numbers of β -rhomb-B and tetra-B. Calculated values are taken from the synthesized interference function by the least-squares variational method.

Table I Atomic distances and coordination numbers for a-B together with the values for β -rhomb-B and tetra-B

	1st peak		2nd peak		3rd peak	
	r [nm]	N	r [nm]	N	r [nm]	N
a-B	0.176	5.6	0.250	2.3	0.299	13
β -rhomb-B	0.180	6.4	0.249	0.4	0.307	15.8
tetra-B	0.182	7.5	0.244	1.7	0.305	15.7

interference function is then systematically refined to yield a satisfactory fit to the observed one using a non-linear least squares method, and the atomic distances and coordination numbers are determined by this procedure.⁹ This method is useful because one need not consider the truncating effect with Fourier transformation. The atomic distances and coordination numbers of β -rhomb-B and tetra-B listed in Table I were calculated from the results of structure analysis by G. A. Slack et al.⁹ and M. Vlasse et al.⁹ The atomic distances were obtained as mean values in the range of 0.15-0.21 nm, 0.21-0.27 nm, and 0.27-0.34 nm. And the corresponding coordination numbers were also obtained as the sum total in those ranges.

While the first and the third peaks observed for a-B can be reproduced by both β -rhomb-B and tetra-B, the second one can be reproduced by the latter better than the former. It has been reported that the inter-cluster bonds between B_{12} clusters in a-B are considered to be not "in phase" but "out of phase".¹⁰ However, the atomic linkages corresponding to the second peak for a-B are not found in either "in phase" or "out of phase". The second peak for tetra-B is derived from "pseudo out of phase" and a linkage between an atom in B_{12} clusters and an isolated atom. Therefore, it is probable that the

inter-cluster bonds between B_{12} clusters are "pseudo out of phase" and/or the isolated atoms are present in a-B. However, since the structure analysis results of tetra-B⁹ are not reliable (we have found physically impossible short distances in the structure, such as 0.019 nm), we can not make it clear. B_{12} hard spheres random-packed model calculation by R. G. Delaplane et al.¹¹ has expressed the second peak, and the present results support their calculation.

Figure 5 shows the RDF for a-16at%Si together with the coordination numbers of crystalline B_6Si ($B_{15.2}$ at%Si),¹² which has approximately the same silicon concentration as a-16at%Si. Table II shows the atomic distances and coordination numbers of c- B_6Si , a-16at%Si, and a-Si. The atomic distances and coordination numbers of c- B_6Si are the mean values and the sum total in the range of 0.16-0.24 nm, respectively.

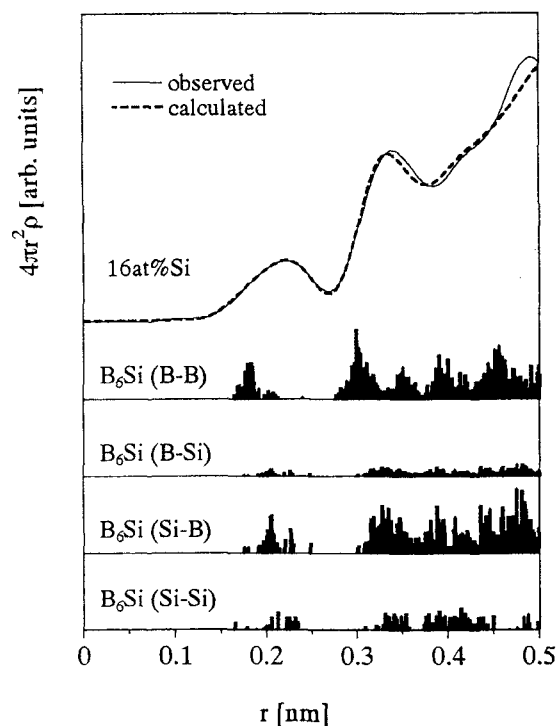


Fig. 5 Radial distribution function for a-16at%Si and coordination numbers of c- B_6Si . Calculated values are taken from the synthesized interference function by the least-squares variational method.

Table II Atomic distances and coordination numbers for a-16at%Si and a-Si together with the values for c- B_6Si .

	c- B_6Si		a-16at%Si		a-Si	
	r [nm]	N	r [nm]	N	r [nm]	N
B-B	0.182	5.3	0.182	5.5		
B-Si	0.206	0.76	0.206	0.66		
Si-B	0.206	4.3	0.206	3.6		
Si-Si	0.216	1.4	0.234	2.5	0.234	3.3

Those of a-16at%Si were calculated using the least-squares variational method, and those of a-Si were evaluated by Gaussian function fitting to the RDF for a-Si.

Although the atomic distances of B-B and B-Si pairs for a-16at%Si are almost the same as those for c-B₆Si, the coordination number of B-Si pairs decreases from 0.76 for c-B₆Si to 0.66 for a-16at%Si. On the other hand, the coordination number of Si-B pairs decreases from 4.3 for c-B₆Si to 3.6 for a-16at%Si, and that of Si-Si pairs increases from 1.4 to 2.5. The results show that, on the average, one of boron atoms around a silicon atom in the structure of c-B₆Si is replaced by one silicon atom in a-16at%Si.

The structure of c-B₆Si contains icosahedra (M₁₂ clusters), icosihexahedra (M₁₅ clusters), as well as several isolated atoms, where M is B or Si atom; and it is also principally constructed with the clusters.¹²⁾ For a-16at%Si, by adding the coordination number of Si-B pairs to that of Si-Si, one find that the coordination number of Si is 6.1. This value is much closer to that for c-B₆Si of 5.9 than that for a-Si of 3.3. It indicates that the structure of a-16at%Si is not random network similar to the structure of a-Si but principally constructed with the same clusters as c-B₆Si. It agrees with that the X-ray diffraction pattern of a-16at%Si is categorized into that of a-B in Fig. 2.

Absorption coefficients, α , in many amorphous materials have been observed to obey the following relation above the exponential tails:¹³⁾

$$\alpha h\nu = A(h\nu - E_{opt})^n \quad (1)$$

where $h\nu$ is photon energy and A is a constant. A constant, E_{opt} , is defined as an optical band gap. The absorption coefficients, α , have been usually better-fitted with the exponent $n=2$ for the amorphous semiconductors with rather simple structure, such as a-Si and a-As₂S₃. They have been usually better-fitted with $n=3$ for the amorphous semiconductors with rather complicated structure, such as a-B and multi-component chalcogenide glasses.⁵⁾ Accordingly, The absorption coefficient of a-Si was fitted with $n=2$ and that of a-B

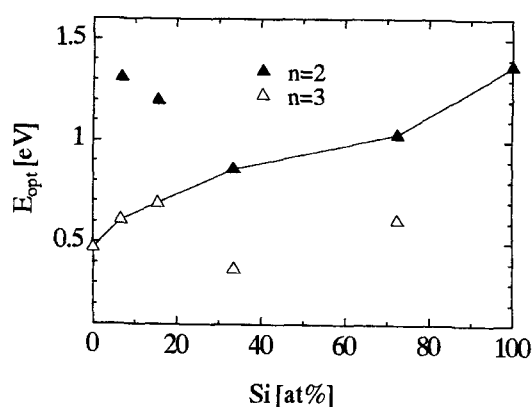


Fig. 6 Si concentration dependence of optical band gap both with $n=2$ and with $n=3$

was fitted with $n=3$, and the optical band gaps were evaluated (Fig. 6). Figure 6 shows Si concentration dependence of the optical band gaps derived by fitting with $n=2$, and also that with $n=3$. Although the absorption coefficients are fitted well and correlation coefficients are more than 99 % in any case, it is reasonable to suppose that the absorption coefficients are fitted with $n=3$ in the composition range less than 16 at%Si and they are fitted with $n=2$ in the range more than 34 at%Si. It corresponds to that the X-ray diffraction patterns are divided into the two groups between 16 at%Si and 34 at%Si in Fig. 2.

Above the tail of the conduction band and below the tail of the valence band, the density of states has a parabolic distribution for the amorphous semiconductors better-fitted with $n=2$. Both the slope and curvature of the density of states for the amorphous semiconductors better-fitted with $n=3$ are smaller than those with $n=2$.⁵⁾ It indicates a change in the band edge structure of B-Si amorphous films between 16 at%Si and 34 at%Si (from the parabolic distribution to the straight distribution).

From the above results, the following is suggested. The structure of the boron-rich amorphous phase, constructed with clusters, such as B₁₂ clusters, changes to the random network similar to the structure of a-Si at around 20 at%Si. At the same time, the characteristic optical absorption edge spectrum, that is the characteristic density of states at the band edges, for the amorphous semiconductors with complicated structure changes to that with rather simple structure. For the purpose of making it clear, we are planning to do detailed experiments.

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