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Electron-beam deposited boron coatings for the extreme ultraviolet

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Abstract

B films deposited by evaporation with an electron-beam were found to have a relatively high reflectance in the extreme ultraviolet (EUV), with values similar to those of ion-beam-sputtered (IBS) SiC and IBS B_4C. The largest reflectance was measured for an 11-nm thick B film. Some reflectance degradation was observed for B films stored in a desiccator. Reflectance degradation varied from sample to sample, and it was found to be either similar to that of IBS SiC and IBS B_4C or larger.

OCIS Codes: 260.7200, ultraviolet, extreme; 260.7210, ultraviolet, vacuum; 230.4040, mirrors; 310.6860, thin films, optical properties; 230.4170, multilayers

1. INTRODUCTION

Mirrors for the spectral region below the LiF cutoff wavelength (105 nm) are burdened with the relatively low normal reflectance of all known stable materials. Al films, which is the material with the largest reflectance above ~83 nm, are degraded upon exposure to atmosphere; no protective coating that is transparent below 105 nm is available to prevent this degradation. Standard multilayers are hindered by the strong absorption of all materials in the ~50-105 nm range, that will be referred to here as extreme ultraviolet (EUV), so that single layer coatings are mostly used in this range**;** only recently some multilayer coatings have been developed for this range[1,2,3,4,5,6]. Mirrors with high reflectance in the EUV are necessary for several applications. The observation of the universe at fundamental spectral lines lying in the EUV is usually complicated due to the low intensity of the sources and to the modest reflectance of the coatings. High reflectance EUV mirrors are required also for other applications, including plasma diagnostics, spectroscopy, synchrotron radiation, and free electron lasers.

A small set of reflective materials is available for mirror coatings in the EUV. Chemical vapor deposited (CVD) SiC[7] is the stable material with the highest normal reflectance in the EUV down to 60 nm, with values around or above 40%. Bulk hot-pressed B_4C[8] extends the relatively high reflectance in the EUV down to 49 nm. Thin films of different materials deposited by physical vapor deposition, like SiC prepared by magnetron sputtering[9] and by ion-beam-sputtering (IBS)[10], IBS B_4C[11], or evaporation-deposited Ir[12] have somewhat lower reflectance than the above. IBS films are often advantageous because they involve low substrate temperature processes and are cost-effective. Ir layers are used to reflect the ~49-65 nm range; best

evaporation-deposited Ir films require deposition over substrates heated at least at ~540 K[12,13]). The development of new coating materials with high reflectance in the EUV is important both to increase the spectrum of reflective materials and also to use them as components of sub-quarterwave multilayers[1,2].

SiC, B_4C, and C are among the materials with moderately high reflectance in the EUV. B, being the main component of B_4C, has been considered a candidate material for high EUV reflectance. A characteristic of B is that it can be deposited by evaporation, differently to SiC and B_4C, which are best deposited by sputtering because evaporation affects their stoichiometry.

No data was found in the literature on the EUV reflectance of B, either in situ or exposed to the atmosphere. In the EUV, only transmittance measurements were found. Labov *et al.*[14] measured the transmittance in the 5.4-248 eV spectral range of a B film that had been exposed to the atmosphere. Fernández-Perea et al. [15] investigated the transmittance of B films deposited in situ in UHV in a broad range including the EUV, and calculated the optical constants of B.

This paper reports on the reflectance of B films deposited by electron-beam over room-temperature substrates. The paper is organized as follows. Section 2 describes the experimental techniques used in this research. Section 3 displays the reflectance of B films of various thicknesses and the reflectance degradation upon exposure to atmosphere.

2. EXPERIMENTAL TECHNIQUES

Samples were prepared in an ultra-high vacuum (UHV) system that basically consists of a thin-film deposition chamber connected in vacuum to an EUV reflectometer. Absolute reflectance measurements can be performed *in situ*, i. e. on freshly deposited samples that are maintained continuously in UHV conditions. The reflectometer-deposition system has been described elsewhere [16], [17]. Each chamber was pumped with an ion pump and a titanium sublimation pump. Both the deposition and the reflectometer chambers were baked at 470 K. The base pressure both in the deposition chamber and in the reflectometer was ~$2x10^{-8}$ Pa. The total pressure in the reflectometer during reflectance measurements, i.e. with the reflectometer connected to the lamp-monochromator, was ~$1.5x10^{-7}$ Pa.

We evaporated 99.7% pure crystalline B from Aldrich by means of a 6-kW electron gun provided with a pyrolytic graphite liner placed in a Cu crucible. Pressure during evaporation was ~1×10^{-6} Pa, and deposition rate was 2.2 – 2.8 nm/min. B film thickness was monitored with a quartz crystal oscillator, that had been previously calibrated through Tolansky interferometry[18]. Tolansky interferometry was used also to measure the film thickness a posteriori. B films were deposited over glass substrates. The uncertainty in the film thickness determination through Tolanski interferometry was estimated to be ±1 nm. The substrates were not intentionally either heated or cooled during deposition.

Reflectance measurements were performed over samples at room temperature. A CsI-coated channel electron multiplier was used as the EUV radiation detector. Reflectance

measurements were performed as follows. A thin film of B was deposited in the deposition chamber and transferred in vacuum to the reflectometer. The sample was alternately placed in the way of the beam at a normal angle of 5º and removed from the beam direction; the detector was rotated to measure the reflected beam and the direct beam. The average of several reflected-to-direct beam intensity ratios was taken as the reflectance at each wavelength. Once the reflectance of the freshly deposited samples was measured, they were removed from vacuum, stored in a desiccator and their reflectance was remeasured after several storage periods.

3. RESULTS AND DISCUSSION

Fig. 1 displays the reflectance of freshly deposited B films of thicknesses ranging from 11 to 40 nm. A relatively high reflectance is obtained with all three thicknesses. The 11-nm thick film provides a larger reflectance at long and at short wavelengths. In the central range, the three thicknesses resulted in a close reflectance. The larger reflectance of the thinnest film at some spectral ranges is attributed to constructive interferences between waves reflected at the vacuum-B and the B-glass interfaces; the important absorption of B in this spectral range[15] reduces the reflected field at the second interface with increasing film thickness. This absorption is maximum in the central range of Fig. 1 and decreases away, so that a reflectance increase due to constructive interference is obtained on the two extreme ranges. The reflectance uncertainty is estimated to be $\Delta R=\pm 0.002\pm 0.02R$, where R means the exact reflectance.

Fig. 1 also plots the reflectance calculated with the optical constants *n*, *k* published in Ref. 15. In this calculation, an opaque B film was assumed in order to avoid the

influence of the substrate. Best agreement in reflectance is obtained with the thickest film, as it is expected since the latter minimizes the interference with the substrate. The agreement with the 40-nm thick film is good below ~150 nm, except at 53.6 and at 113.5 nm. At short wavelengths such as 53.6 nm B extinction coefficient starts decreasing, which may result in some contribution to reflectance from the inner B film-substrate interface in the 40-nm thick film. At 113.5 nm that contribution is negligible; the deviation is attributed partly to reflectance measurement error and partly to optical constant inaccuracies, which probably took large and opposite values. The larger deviation at wavelengths longer than 150 nm is mostly attributed to inaccuracies in the optical constants used, as it is explained in the following. k was calculated in Ref. 15 from transmittance measurements of samples prepared in situ in UHV. However, n was calculated from a set of k data that combined the above k data with data in the literature and extrapolations in the spectrum that was not measured. In Ref. 15, no k data was produced at wavelengths between 182 and 365 nm, so that an interpolation between the data of Ref. 15 and the works of Morita[19] and Morita and Yamamoto[20] was performed. If this interpolation resulted in inaccurate k data, this inaccuracy would propagate to the calculation of n through Kramers-Kronig integral mainly in the close spectral range, such as in the current 150-180 nm.

Fig. 2 compares the reflectance of the 11-nm thick B film that is plotted in Fig. 1 with that of IBS SiC[21], IBS B_4C[22], IBS C[23] and bulk Si[24]. B is found to have a relatively high reflectance close to those of IBS SiC and IBS B_4C. IBS C converges to these materials at short wavelengths. Si has a lower short-wavelength reflectance, and a higher long-wavelength reflectance. Fig. 2 suggests that combinations of Si, C and B, such as boron silicides, might also have a high reflectance in the EUV.

The above data of Figs. 1 and 2 correspond to B films that had not been exposed to atmosphere. Figs. 3 and 4 display the degradation of B reflectance upon ageing in a desiccator (except the 18 min. exposure, which was given under normal atmosphere); Figs. 3 and 4 were obtained for 11- and 33-nm thick B films, respectively. The thicker film suffers from a larger degradation than the thinner film. This difference in ageing is not well understood, and hence we suggest that it might be at least partly due to variations from sample to sample. In fact, Fig. 3 results in an aged B reflectance comparable to those of aged IBS SiC and IBS B_4C[1], whereas the reflectance decay in Fig. 4 is larger. The extent of B film oxidation was previously characterized through X-ray photoelectron spectroscopy[15]. A boron suboxide was detected to grow on the surface of aged B films, and no oxide was detected after removing a layer of about 2 nm. Hence the exposure to atmosphere results in some oxidation, which does not extend deep. This low depth oxidation agrees with the observed limited reflectance degradation.

Reflectance degradation is often enhanced due to the presence of voids in the film. A low packing density, related with voids and defects in the film, may turn the material more prone to react with gases of the atmosphere. A 2.1 g/cm^3 density was measured for B films in [15], which results in a packing density of 90%. The observed B reflectance degradation for films deposited by evaporation is either similar that or somewhat larger than for IBS SiC and IBS B_4C. In principle, it may be expected that films deposited by sputtering may have larger packing density than films deposited by evaporation, due to the former larger atom mobility at the growing surface. A larger packing density, and hence a smaller degradation, might then be predicted for B films deposited by

sputtering, although no information was found to assert this; hence, a research focused on the reflectance of B films deposited by sputtering might be an interesting continuation line of the present research.

4. CONCLUSIONS

B films deposited by electron-beam evaporation were found to have an EUV reflectance as high as films of SiC and B_4C deposited by sputtering. The largest reflectance was measured for an 11-nm thick sample. A high reflectance is observed for the three elements B, C, Si, and their compounds SiC and B_4C, which suggests that boron silicides are candidate materials for high EUV reflectance. An interesting characteristic of B films is that they can be deposited by evaporation, differently to SiC and B_4C, which are deposited by sputtering because their stoichiometry is modified by evaporation.

Some degradation was observed for the reflectance of B films after months of storage in a desiccator. One specific sample resulted in a similar degradation to IBS SiC and IBS B_4C, whereas another sample degraded more. More research would be necessary to precisely establish the long-term reflectance degradation of B films.

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FIGURE CAPTIONS

Fig. 1. (Color online) Reflectance versus wavelength of freshly deposited B films of three different thicknesses. The calculated reflectance of an opaque B film is also plotted.

Fig. 2. (Color online) Reflectance of a freshly deposited B film compared with the reflectance of IBS SiC [21], IBS B_4C[22], IBS C[23] and bulk Si[24].

Fig. 3. (Color online) Reflectance of an 11-nm thick B film both freshly deposited and after a storage of 6 months in a desiccator

Fig. 4. (Color online) Reflectance of a 33-nm thick B film both freshly deposited and after several storage periods in air and in a desiccator

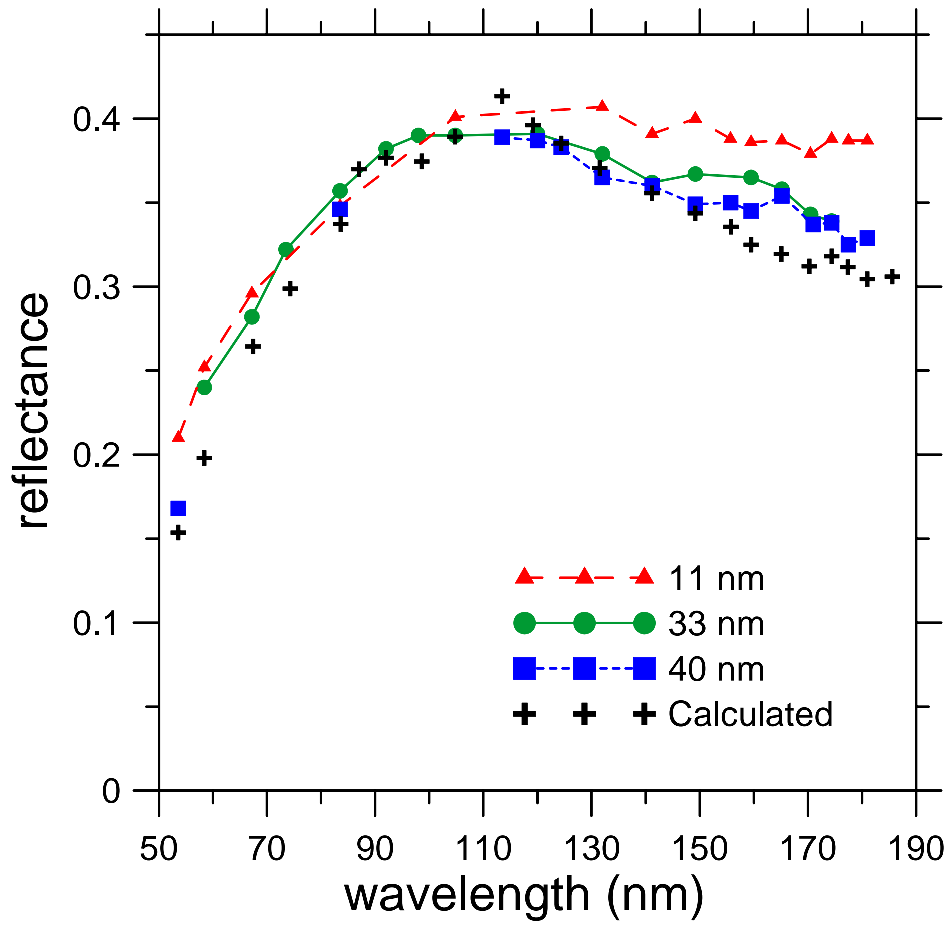

Fig. 1

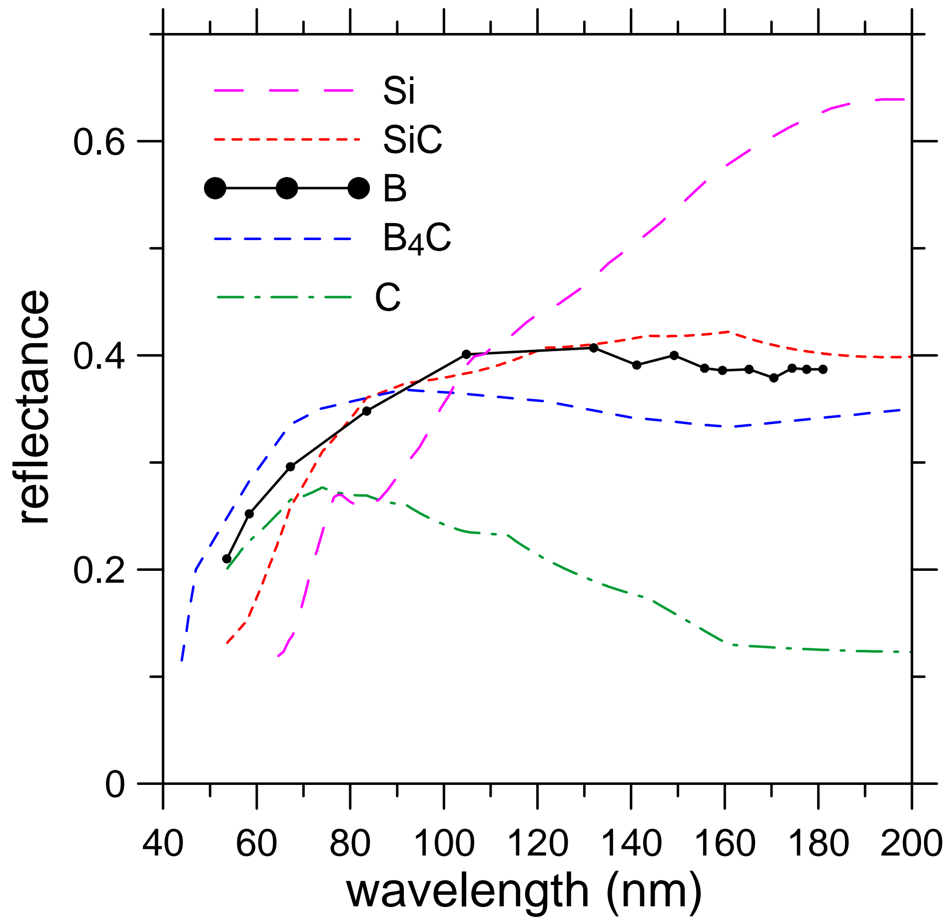

Fig. 2

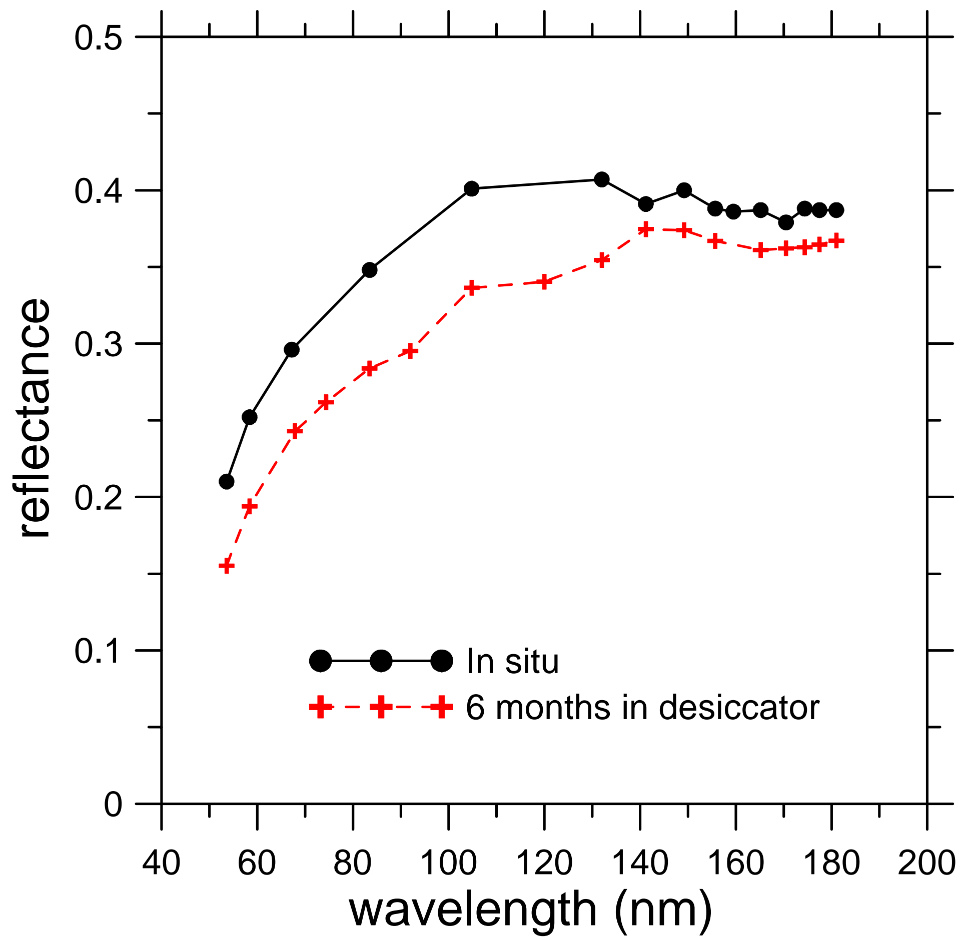

Fig. 3

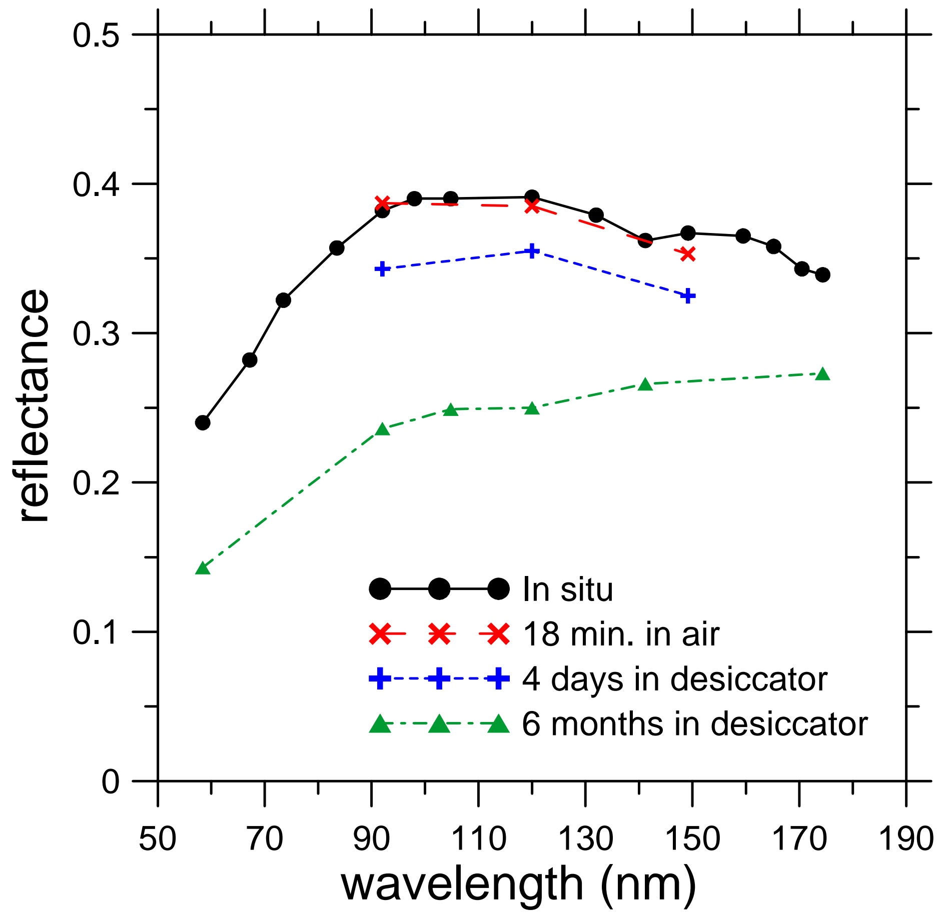

Fig. 4