The role of beryllium deuteride in plasma-beryllium interactions

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ABSTRACT

Beryllium deuteride has been measured in plasma-exposed surfaces and in the plasma column of the PISCES-B experiment. XPS measurements of high-purity BeH_2 samples, used as standards, confirm the presence of beryllium deuteride in beryllium codeposited material (Be 1s energy of BeH_2 bond = 115.0 eV). TDS measurements of high-purity BeD_2 samples are used to accurately determine the decomposition temperature of the beryllium deuteride molecule ($\sim$540 K). Deuterium release is observed from plasma-exposed beryllium samples and from Be codeposited layers at this temperature. BeD molecular (A–X) band emission is observed in beryllium seeded plasma discharges and during deuterium sputtering measurements of beryllium. Band emission intensities during Be-seeding are used to estimate the photon emission coefficient, $<\sigma v>$, for the band. The $<\sigma v>$ value verifies that molecular sputtering of BeD (from beryllium targets saturated with deuterium from the plasma exposure) is a small fraction of the physical sputtering of beryllium atoms.

1. Introduction

The formation of metal hydrides could be a serious concern for plasma confinement devices utilizing tritium as part of its fuel gas. The bonding of hydrogen isotopes to elements used as plasma-facing materials can significantly increase tritium retention and may be important in devising techniques necessary to remove the accumulated tritium once an on-site accumulation limit is reached. The plasma-material interaction community is well aware of the issues associated with the formation of hydrocarbons in fusion devices [1], but is much less aware of the potential issues associated with the formation of beryllium–hydrogen bonds.

Beryllium hydride (BeH_2) and its deuterated sibling, beryllium deuteride (BeD_2), are of interest to basic science researchers because of their relatively small number of electrons (6) and the large mass difference between the two isotopically differing molecules (18%). Solid beryllium hydride is most commonly produced through a complicated controlled pyrolysis of beryllium-containing ethers [2], although it has also been condensed on cryogenic surfaces using laser ablated beryllium atoms in a hydrogen atmosphere [3]. Infrared signatures of the gaseous BeD_2 and BeD molecules have also been investigated using an electrical discharge in a high temperature furnace during hydrogen gas flow [4,5]. Even the beryllium tritide molecule has been experimentally investigated [6].

Beryllium deutertide has been proposed as the ablator material in inertial confinement targets [7]. In the field of magnetic fusion, the BeD molecule has been observed being sputtered from the target plates in the JET divertor [8].

In this paper, we report on the effort in the PISCES-B device to understand the importance of the beryllium deuteride molecule in plasma-surface interactions with beryllium targets, the role of beryllium deuteride in codeposited layers and the role of gas phase reactions resulting in the formation of beryllium deuteride during beryllium-seeding experiments. This work was greatly aided by the generous donation of separate high purity (>95%) samples of BeD_2 and BeH_2 [9,10] by Professor J. Yarger at Arizona State University to be used as standards for comparison to surfaces created during plasma exposure.

2. Signatures of beryllium hydride standards

The beryllium hydride sample was used to obtain XPS spectra for comparison with beryllium layers deposited by the PISCES-B beryllium-containing deuterium plasma as described in other publications [10,11]. No line shift data was available in the literature for the BeH_2 bond, so the BeH_2 powder was coated onto carbon tape and inserted into the XPS analysis station. The resultant XPS spectrum is shown in Fig. 1(a). Also shown in Fig. 1 are the XPS spectra from beryllium targets exposed to helium plasma (1d) and deuterium plasma (1c) along with the spectrum from a beryllium codeposited layer (1b). The spectrum from the helium bombarded sample (1d) is used to obtain the position and full width at half maximum of the Be metallic and oxide peaks. The location
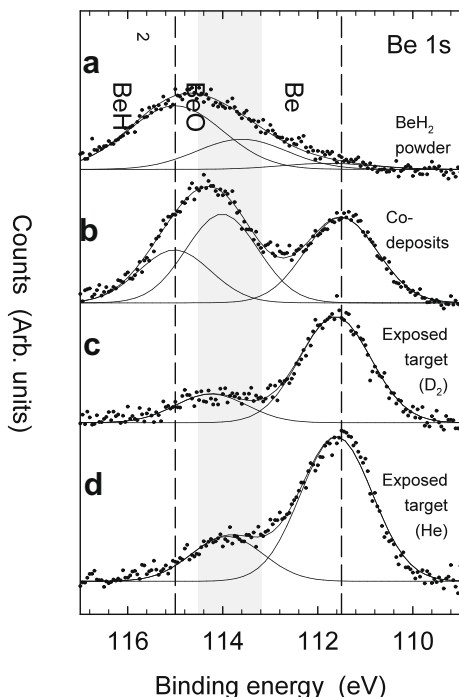
Fig. 1. Deconvolution of XPS Be 1s spectra from BeH_2 powder (a), codeposited Be layer (b), Be target exposed to D plasma (c) and Be target exposed to He plasma (d). The spectra are fit with Be metallic (111.5 eV), Be oxide ($\sim$114 eV) and Be hydride (115.0 eV) Gaussian peaks.

and half-widths of the peaks are used as the calibration of the energy scale for the other spectra shown. The same two peaks provide a good fit to the deuterium plasma-exposed sample (1c), indicating that the quantity of BeD_2 molecules existing in the surface is below the XPS detection limit. The spectrum from the Be codeposit (1b) cannot be fit with only the two (metallic and oxide) peaks. A third peak is needed in this fit. The energy of the third peak corresponds to that of a third peak needed to fit the spectrum obtained from the BeH_2 standard (1a). The energy attributed to the Be–H_2 bond is 115.0 ± 0.1 eV.

The XPS analysis indicates that while the amount of beryllium hydride bonds forming in plasma-bombarded surfaces is small, the amount of hydrides forming in codeposited layers is significant. In retrospect, this is not surprising since there is little difference between our codeposition experiment and condensation of laser ablated Be in a hydrogen atmosphere [3].

XRD analysis was attempted on Be layers deposited at $\sim$350 K and $\sim$640 K, but no discernible signals that could be related to crystalline BeD_2 [12] were observed. This could indicate that any BeD_2 created is in an amorphous form, or that the content in the samples is too small to be observable.

The standard beryllium deuteride sample was used to generate the expected decomposition trace obtained using thermal desorption spectrometry (TDS). BeD_2 decomposes by releasing the D_2 molecule and leaving Be residue. In other words, BeD_2 decomposes into its elemental constituents before it reaches a temperature where it becomes volatile. To ensure uniform heating of the BeD_2 powder, it was inserted into a small Ta crucible that was used inside the TDS oven as a blackbody radiator. The heating ramp rate was set to 0.1 K/s. A thermocouple was also inserted into the crucible to provide more accurate temperature measurements during the desorption process. As can be seen from Fig. 2, a small amount of D_2 begins being released when the sample is heated above 330 K, but the primary deuterium release peak occurs at $\sim$540 K. The temperature of this release peak agrees with the small low-

temperature release peak observed from beryllium targets exposed to deuterium plasma bombardment at room temperature [13] indicating that small amounts of BeD_2 may have formed in the plasma-exposed surfaces. Of course, after higher temperature ($\sim$725 K) plasma exposures this release peak is not observed [13]. A deuterium molecule release peak, at a similar temperature, is also observed from beryllium codeposited layers [14] that are deposited at temperatures less than the decomposition temperature of BeD_2.

The comparison of TDS signals from surfaces interacting with plasma to those of known beryllium deuteride standards is consistent with a small amount of BeD_2 existing in beryllium samples exposed to deuterium plasma, consistent with the XPS results. The XPS result indicating BeD_2 bond formation in codeposited Be layers is confirmed by the TDS analysis.

3. Observation of BeD emission from the plasma

There is also evidence for the existence of beryllium deuteride molecules in the PISCES-B plasma. Two separate types of experiments observe BeD molecular band emission from the plasma. First, a beryllium-filled effusion cell is used to inject beryllium into deuterium plasma [15] (an experimental system not unlike that of [4]). The BeD molecular band emission (A–X band $\sim$ 490–507 nm) is observed to radiate throughout the plasma column. Since there appears to be no cross-section data available to quantify the amount of the molecule present in our plasma, an experiment was performed to obtain an estimate of the photon emission coefficient, <σv>. In these measurements, BeD molecules are thought to be created by beryllium ions reacting with deuterium molecules resulting in either BeD molecules and deuterium ions, or BeD ions and deuterium atoms. Since the D_2 density is more than 2 orders of magnitude larger than the D_2^+ density, the reaction of D_2^+ ions with Be atoms is neglected.

While the plasma conditions ($n_e = 3.5 \times 10^{18}$ m^{-3}, $T_e \sim 7$ eV) and the beryllium oven temperature were kept fixed, the deuterium fill pressure within the device was increased from 5 to 10 mTorr. As a result of this change the measured beryllium ion density decreased from 5 to 1.5×10^{15} m^{-3} while the BeD band emission, integrated from 497.3 to 499.2 nm, increased from 100 to 260 $\times 10^{16}$ photon/s m^2 sr. Assuming the conservation of beryllium atoms, singly ionized beryllium ions and BeD molecules, we

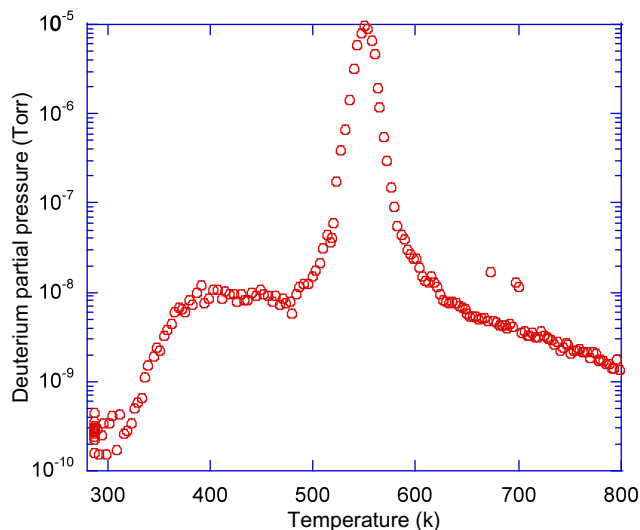**Fig. 2.** TDS spectra of BeD_2 powder showing decomposition and release of deuterium at $\sim$540 K.

obtain a value of $\langle\sigma v\rangle_{BeD} \sim 5 \times 10^{-14}$ m^3/s. This value for $\langle\sigma v\rangle_{BeD}$ should be treated as a lower limit, as some amount of BeD$^+$ might also be expected to form.

In the second type of measurements, as described in [16], BeD molecular band emission is observed directly in front of beryllium targets exposed to deuterium plasma bombardment. During these measurements, this BeD emission resulting from sputtering of the molecule from the target surface is measured to drop by more than a factor of two as the temperature is increased beyond the decomposition temperature of BeD$_2$ as shown in Fig. 3(a). Also shown in Fig. 3(b) is the BeI atomic emission during the same temperature variation experiment. It is possible that the small decrease in the BeI emission with the increased temperature may be due to a change in the amount of BeD disassociating near the sample surface.

The spectroscopic data shown in Fig. 3, along with the $\langle\sigma v\rangle_{BeD}$ obtained above, can be used to estimate the change in the temperature dependent flux of BeD molecules leaving the beryllium sample surface compared to the flux of beryllium atoms leaving the surface. Assuming the velocity of BeD molecules and Be atoms sputtered from the surface are similar, the flux of each is proportional to the axially integrated intensity divided by the $\langle\sigma v\rangle$ of each transition. The ratio of the change in molecular to atomic flux leaving the surface, F, is

$$F = (\Delta I_{BeD} * \langle\sigma v\rangle_{BeI})/(I_{BeI} * \langle\sigma v\rangle_{BeD}) \sim 0.18 \qquad (1)$$

where the ADAS [17] value of $\langle\sigma v\rangle_{BeI} = 3 \times 10^{-15}$ m^3/s has been used.

Previous measurements [18] have documented that beryllium samples exposed to deuterium plasma at high fluence (over 1×10^{26} m^{-2}) have no temperature dependence of the sputtering yield (obtained from mass loss measurements) over the temperature range from 323 to 923 K. This ratio of molecular to atomic flux obtained here, which is an upper bound, is within the measured uncertainty in the previous experiments.

4. Discussion

The presence of beryllium hydride, or more accurately beryllium tritide, may at first glance appear to be a concern from the point of view of tritium retention in future fusion experiments. However, there are several factors that tend to mitigate its importance. First, it is non-volatile, so unlike the hydrocarbon species, it does not lead to chemical erosion and therefore does not promote the migration of tritium to locations away from line of sight of its creation point. An RGA located with non-line-of-sight of the PISCES-B plasma has never detected any beryllium-containing species during plasma operations. In addition, the decomposition temperature of beryllium hydride is fairly low (540 K) so any tritium bound with beryllium can be easily recovered at a fairly modest baking temperature. And finally, although it appears to play a more prevalent role in codeposited layers, as compared to surfaces in direct contact with plasma, in neither case does it appear to dominate the plasma-surface interactions with those surfaces.

The creation of BeD molecules in the plasma due to the operation of the Be-seeding oven in PISCES-B does have to be taken into account during mixed-material studies, as it leads to an additional channel for beryllium to arrive at the target surface. During normal plasma operation with Be-seeding, the deuterium background pressure is typically 6 mTorr, the electron density $\sim 4 \times 10^{18}$ m^{-3} and the electron temperature is approximately 7 eV. At these conditions, the quantity of BeD molecules (neutrals plus ions) is roughly equivalent to the amount of beryllium ions measured in the plasma column. Although this factor of two increase in the arrival rate of beryllium to the plasma-exposed surface needs to be included in the interpretation of experiments, it is not significant enough to alter the conclusion that surface chemistry effects need to be included to understand the mixed-materials studies [9] being conducted at the PISCES Laboratory.

5. Conclusion

The presence of beryllium deuteride has been confirmed in Be codeposited layers as well as in the plasma column of the PISCES-B experiment. XPS measurements of high-purity BeH$_2$ samples, used as standards, show the energy of the BeH$_2$ bond to be 115.0 eV and confirm the presence of beryllium deuteride in the surface of beryllium codeposits. TDS measurements of high-purity BeD$_2$ samples are used to accurately determine the decomposition temperature of the beryllium deuteride molecule (~ 540 K). Deuterium release is observed from plasma-exposed beryllium samples as well as from Be codeposited layers at this temperature.

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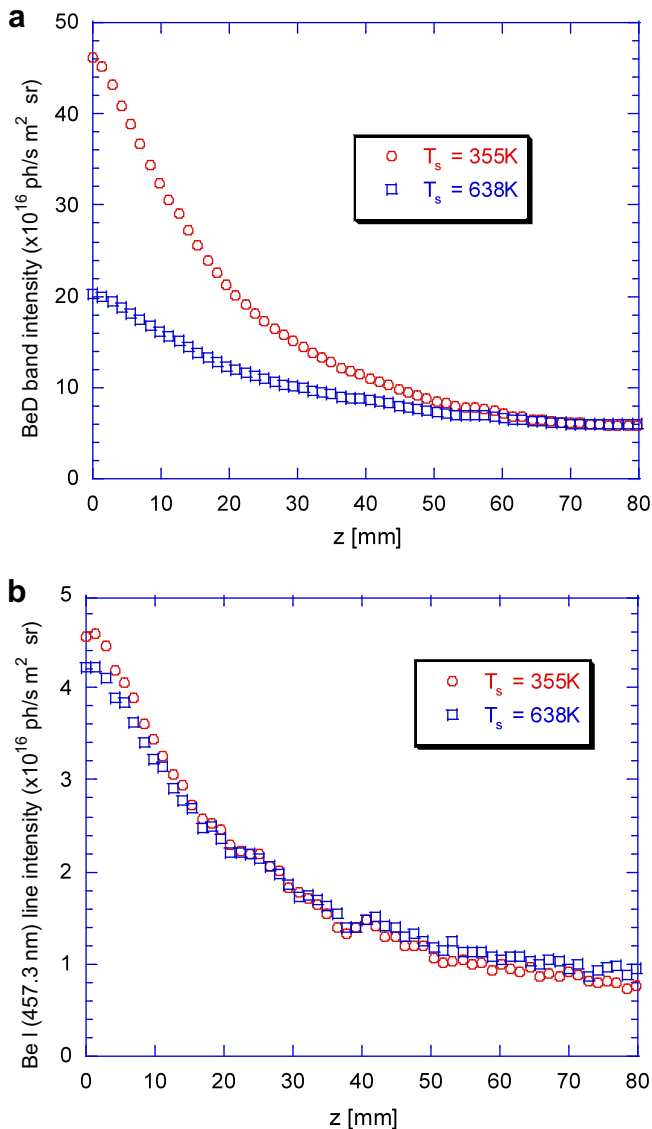

Fig. 3. Axial profiles of (a) BeD band emission and (b) BeI line emission at different Be sample exposure temperatures.

emission coefficient, <σv>, for the band and to estimate the density of molecular species in the plasma. The <σv> value is also used to verify that molecular sputtering of BeD (from beryllium samples saturated with deuterium from the plasma exposure) is a small fraction of the physical sputtering of beryllium atoms.

Acknowledgements

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