Atomic ordering at an amorphous/crystal interface

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In this study, the authors report atomic-resolution images that illustrate the transition from a crystalline Si_3N_4 grain across the interface into an amorphous Lu–Si–Mg–N–O glassy phase. The interface is not atomically abrupt, but is comprised of sub-nanometer-scale ordered regions that resemble a LuN-like structure. These ordered clusters bind to the prismatic surface of the Si_3N_4 grains at specific low energy positions for Lu adsorption as predicted by first-principles calculations. The ordered regions are filamentary in nature, extending for at least two atomic layers into the amorphous pockets at multigrain junctions before disappearing. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2245212]

Amorphous/crystalline interfaces are of critical importance in many technological areas, from semiconductor devices to advanced ceramics.[1–3] However, to date, little is known on the nature of the spatial transition from a bulk amorphous structure to a crystal. It is clear that an abrupt transition from an ordered crystal to an amorphous structure is not realistic. Computer simulations have predicted transition structures for the Si/SiO_2 interface[4] and for the $Si_3N_4/(Ca)-Si-N-O$ interface.[5] However, little experimental data exist to confirm the occurrence of these transition structures.

In Si_3N_4 ceramics, intergranular phases, especially their interface with crystalline grains, have a critical effect on the microstructural evolution and mechanical properties,[2,6,7] and thus controlling interface structures is a key engineering factor. Here, the interface region between Lu–Si–Mg–N–O amorphous pockets and the prismatic surface of the β-Si_3N_4 grains was directly imaged using aberration-corrected *Z*-contrast scanning transmission electron microscopy (STEM) with subangstrom resolution,[8] which has proven to be a very powerful method for characterizing amorphous/crystalline interfaces in ceramics.[9–11] The presence of unique Lu configurations at the Si_3N_4 grain surfaces has been experimentally suggested by previous STEM work.[11] The work indicates the presence of some transient structure across the interface, but the structural details and their formation mechanism are still unresolved.

The detailed fabrication process of the Lu doped Si_3N_4 ceramics observed in this study has been reported elsewhere.[7] Atomic-resolution images were taken with a dedicated 300 kV (VG Microscopes, HB603U) STEM equipped with aberration corrector (Nion Co.), providing a minimum probe diameter of <0.8 Å.[8] The specimens for STEM observations were prepared by a standard procedure, using ion thinning. A thin amorphous carbon film ($\sim$3 nm) was deposited onto each sample to avoid charging effects.

Figure 1(a) shows a *Z*-contrast STEM image of an interface region between a Lu doped silicon oxynitride amorphous phase and a β-Si_3N_4 crystal. The β-Si_3N_4 crystal on the left side is aligned with the [0001] projection, so that the $(10\bar{1}0)$ prismatic interface plane is in the "edge on" condition. In the *Z*-contrast STEM image, each bright spot within the crystal corresponds to the position of a column of a high number density of Si atoms. As seen in numerous observations by us and others,[9–11] the interface is atomically flat over extended distances along the prismatic crystal surface. In addition, two rows of periodic, very high contrast spots are observed lying parallel to the interface but within the amorphous phase adjacent to the crystal surface. The image intensity profile across the interface in Fig. 1(a) is shown in Fig. 1(b). Subtracting the smoothed background (dashed line)

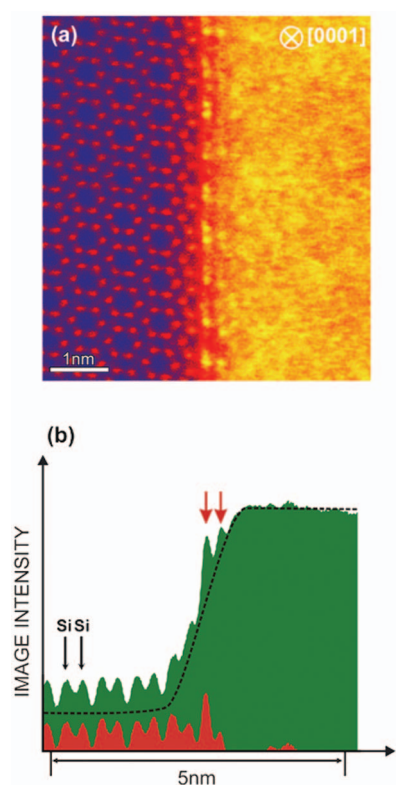

FIG. 1. (Color) (a) Aberration-corrected *Z*-contrast scanning transmission electron microscopy (STEM) image of an interface between β-Si_3N_4 crystal and Lu doped oxynitride glass pocket at multigrain junctions. (b) The image intensity profile across the interface representing the average values for traces parallel to the interface (green profile).

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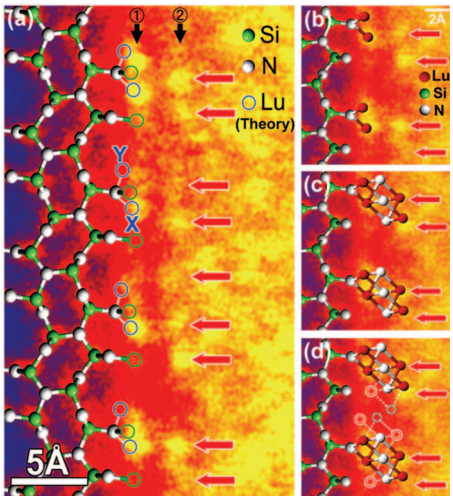

FIG. 2. (Color) Magnified *Z*-contrast STEM images of the interface in Fig. 1. (a) Lu sites in the two rows of strong image intensity (1 and 2) can be clearly resolved. Red arrows indicate the distinct Lu sites in the second row. Lu sites in the first row are in good agreement with theoretically predicted stable Lu sites (open blue circles). Vacant Si sites based on the extension of the β-Si_3N_4 lattice structure are shown by open green circles. [(b)–(d)] Fragments of the LuN crystalline structure of increasing size are superimposed on the STEM images. (b) Lu sites based on the LuN coordination on the (111) plane are superimposed onto the first Lu row, and (c) the extended (111) LuN coordination is superimposed on the second Lu row connected to that in the first row by N. This local LuN-like ordering agrees quite well with observed sites in the first and second Lu rows at the interface. On the other hand, as seen in (d), expansion of the LuN unit to either side of those in (b) and (c) is not observed in the STEM images.

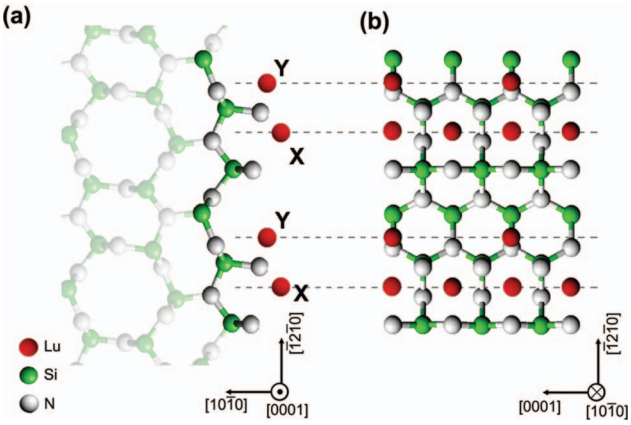

FIG. 3. (Color) Theoretically predicted adsorption sites for Lu on the nitrogen-terminated prismatic surface of a β-Si_3N_4 crystal. The sites are viewed, (a) parallel to the [0001] direction with the $(10\bar{1}0)$ seen edge on and (b) normal to the prismatic surface. For Lu adsorption on this surface, two distinct energy minima per surface unit cell exist along the [0001] projection in the prismatic grain surface at **X** and **Y**.

from the original profile, we find that the peaks associated with the Si columns, which are continuous through the depth of the foil, have constant intensities up to the termination of the Si_3N_4 lattice (red profile). However, the first column in the amorphous phase exhibits higher intensity than that of the continuous Si columns of the Si_3N_4 lattice. This clearly indicates that ordered columns exist at the beginning of the amorphous phase, composed of high atomic number constituent atoms (in this case, Lu). Also, the second layer in the amorphous phase has lower but definite intensity, suggesting gradual structural randomization of Lu order across the interface. In this study, only a single interface that satisfied the orientation conditions was located and characterized, but the observed ordering of the adjoining high intensity spots was detected over extended lengths along the interface (>30 nm). Thus, the ordered structures addressed here should be representative of the stable (ground state) structure of this particular amorphous/crystal interface. In intergranular amorphous films of the same material, similar bright spots were also found at the film/crystalline interfaces.[12] The energy dispersive x-ray (EDX) analysis confirmed the presence of Lu atoms in the film, indicating that the observed intensity spots adjoining the interface indeed correspond to the presence of atoms with high atomic number, in this case, Lu. In this system, confirming EDX data that are strictly from the interface area is difficult to obtain because of beam broadening effects, however, it is plausible that the observed high intensity columns also correspond to the presence of heavy Lu atoms.

Figure 2(a) is a higher magnification *Z*-contrast STEM image of the amorphous/crystalline interface region. Individual Lu sites along the two Lu layers are clearly resolved. Note that the strong intensity Lu spots in the first row appear as dumbbell-shaped doublets or elongated spots and are significantly shifted from the position of Si columns that would occur by extension of the β-Si_3N_4 structure (shown by open green circles). As the underlying β-Si_3N_4 lattice structure illustrates, Lu atoms are attached to the nitrogen-terminated prismatic surface of the β-Si_3N_4 crystal. This finding is consistent with observations and calculations for similar intergranular film/crystal interfaces reported previously for La,[9] and is also supported by independent observations.[10,11] Lu sites in the second row (indicated by red arrows) lie at a constant distance of ~2.8 Å from the first Lu row, indicating the presence of a structural correlation between the first and second Lu rows. Moreover, the Lu sites in the second row exhibit a similar alignment with Lu atoms in the first row [see also Fig. 1(a)]. The positioning suggests a two-dimensional correlation implying that there is likely preferred bonding between atoms in the first and second layers and an intermediate anion plane. Furthermore, the integrated intensity of the Lu sites indicates a column of regular, although lower, number density of Lu atoms. This clearly indicates that the Lu atoms are forming an ordered, filamentary structure in the vicinity of the β-Si_3N_4 crystalline surface. This is also supported by a recent report showing Lu structural order along the [0001] axis.[13]

This interpretation is supported by theoretical predictions of the positions of stable Lu attachment sites on the N-terminated prismatic surface obtained using first-principles cluster calculations. Constructing a surface cluster model including adsorbed Lu, the total energy and restoring forces on each adsorbed Lu atom were calculated using the self-consistent-field partial-wave method.[14] Total energies and forces on the atoms are calculated independently, and they predict the locally stable adsorption sites and resulting structure of the Lu-decorated Si_3N_4 prism plane. The calculations assumed a bare N-terminated surface to focus on the Lu surface interaction. For Lu adsorption on this surface, two distinct energy minima per surface unit cell, **X** and **Y**, are found as shown by the [0001] projection in Fig. 3(a). These sites are superimposed in Fig. 2(a) as open blue circles and designate Lu atoms are aligned in columns on the prismatic surface corresponding to the **X** and **Y** positions. Positions of **X** sites are in excellent agreement with the STEM image,

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while those of **Y** sites show considerably more deviation. Comparison of calculated Lu bond site coordinates with the positions given in Ref. 11 (converted to an origin at the surface double-bonded N atom) is very good for the **X** site. Theory gives **X** site unit cell coordinates (1.82, 1.46) in angstroms, compared with the reported measurement (2.1, 1.6), (4.29, 0.74), and (3.8, 1.5) for the **Y** site.

The contrast of **X** sites is typically higher than that of **Y** sites, indicating higher occupancy of **X** sites than **Y** sites along the z axis. Different intensities in the two sites are found to correlate with the difference in binding energies of Lu to the surface. The binding energy of Lu at the **X** site is calculated to be 0.9 eV greater than that at the **Y** site. Because of the lower binding energy, the positions of Lu atoms on the **Y** sites should be more affected by relaxation of the surface and the adjacent amorphous phase (not included in the present calculation) than the **X** sites, consistent with our STEM observations. The first-principles energetics also suggests that the **Y** column should show a lower atom population density than that of the **X** column along the [0001] axis; this is consistent with our observations of lower intensity at the **Y** positions. The present results indicate that Lu atoms in the amorphous phase have the highest attachment probability for these specific positions (**X** and **Y**) on the N-terminated prismatic surface of the Si_3N_4 crystals. Further calculations of the bond positions of additional Lu and N atoms atop the Lu-decorated prism plane suggest that the second layer Lu pattern could be associated with small Lu-N crystallites.

In order to assess local ordering relationships between Lu atoms in the first and second rows, it is useful to consider models of all known Lu-based structures. One finds that Lu–Lu separation distances and orientations in the cubic LuN structure ($Fm3m$) are comparable to those of the predicted Lu adsorption sites on the Si_3N_4 prismatic surfaces. If we superimpose Lu sites in the LuN structure on those in the first ordered row [Fig. 2(b)], the Lu atoms in the next LuN layer (~2.79 Å away) agree well with the observed Lu sites in the second ordered row [Fig. 2(c)]. This suggests that the two rows indeed involve groups of Lu atoms bonding with nitrogen in an arrangement similar to that found in cubic LuN. However, observations show that the agreement is valid only within islands of two Lu monolayers as depicted in Fig. 2(d). While the comparison reveals that some distortion in bond angles and distances must occur, these are not excessive, bearing in mind that there are also bonds to other atoms in the amorphous Si–Mg–N–O material. This analysis thus indicates that filamentary islands of Lu ordering with LuN crystal-like features are formed at the amorphous/crystalline interface.

The ordering extends at least 5 Å out into the amorphous pockets; while parallel to the interface, the repeat distance of these clusters is dictated by the N-terminated prismatic Si_3N_4 surface, which serves as a template. No evidence is found for a continuous epitaxial LuN layer on the β-Si_3N_4 prismatic plane, but rather 2-monolayers-thick ordered Lu island clusters are formed with a degree of periodicity along the interface. It has been suggested that rare-earth atoms tend to exhibit local ordering or clustering in silicate glasses.[15,16] Thus, the Lu ordering observed at the interface may reflect the atomic-scale influence of adsorbate structural characteristics extending into the amorphous phase, which is then experimentally observable under these unique amorphous/crystalline interface conditions where the interfacial ordering leads to observable variations in intensity in structural probes such as STEM.

The present findings have important implications for understanding the atomic-scale structure of amorphous/crystal interfaces. These results suggest that the stable interface structure is determined by interactions between constituents in the amorphous solid and the structure of the substrate crystal surface, which can allow the formation of local ordered clusters with some crystalline coordination features. Suitable combinations of amorphous compositions and crystal substrates may allow increased control of the interface structure and its width at the atomistic level. Further work is required to distinguish whether the ordered clusters we observe are present within the amorphous material itself. Although they would not be expected to form columnar structures, they might form locally ordered clusterlike regions such as those that have been proposed in the past as the origin of the medium-range ordered structure observed by diffraction. It will be interesting to see if the structure and chemistry of other segregants will also exhibit this templating behavior at the interface.

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