Electron Energy-loss Spectroscopy Characterization of ~1 nm-thick Amorphous Film at Grain Boundary in Si-based Ceramics

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In many ceramic systems thin amorphous films of about 1 nm thickness often cover grain boundaries. These amorphous films play a key role not only in the formation of microstructures but also in the thermal-mechanical properties of ceramic materials. However, such thin amorphous layers could not be probed directly by an analytical electron beam. With the recent advances in spatially-resolved electron energy-loss spectroscopy technique, chemical and physical parameters of the thin films could be successfully derived using the "spectrum separation" approach. Basic characters and behaviors of variations for the inter-granular films are analyzed in a few silicon nitride (Si_3N_4) and silicon carbide (SiC) systems. The combined local chemical-structural information reveal new trends on microstructures and properties, and provides further insights in Si-based ceramic materials.

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1. Introduction

~1 nm-thick amorphous film covering grain boundaries was first observed in 1970's in ceramic materials.^{1,2)} Such amorphous layer explained how densification was achieved in Si-based ceramics where the self-diffusivity within the grains is prohibitively low at sintering temperatures (Fig. 1). Moreover, mechanical properties of these ceramics are strongly affected by such interfacial phases.^{3,4)} A decade later the amorphous films were both rationalized in a specific material as having an equilibrium thickness, which depends only on the sintering additives.^{5–9)} The wetting picture and the force balance model for amorphous film dictated the field until a method of chemical analysis for thin film using electron energy-loss spectroscopy (EELS) was developed in



Fig. 1 HREM micrograph of an amorphous film at grain boundary in $\mathrm{Si}_3\mathrm{N}_4.$

late 1990's.10,11)

This advanced spatially-resolved EELS method, the socalled "spectrum separation" approach, can give a chemical composition and a width of amorphous film in an indirect way, which yields quantitative information from area smaller than electron probe.^{12–14)} The analytical electron microscopy (AEM) results revealed not only that the inter-granular amorphous films in silicon nitride (Si₃N₄) were made of a novel oxynitride phase instead of silica,^{11,15)} but also that such films may have different widths in a given ceramic material, in contrary to the previous high-resolution electron microscopy (HREM) observations.^{15–17)} These observations favor the later diffuse-interface and the multi-layer-absorbate pictures to improve or to replace the wetting picture.^{18–20)}

The new AEM approach on grain boundary has also practical benefits for microstructure researches. The analysis is no longer limited to the few boundaries with high quality 2D projection, which may not be typical in the microstructure. The focus on "guest" (additives and impurities) elements in conventional analysis can also expand to include the "hosts" elements, such as silicon, to reach a more balanced understanding of grain boundary. A quantitative correlation of local interfacial properties with microstructural development and certain macroscopic properties is possible.^{21–23)}

In this paper, I will first describe the EELS "spectrum separation" method that brings the unique information for the inter-granular amorphous films, using a HIPed undoped Si_3N_4 as the model material. In the following sections, other Si_3N_4 and silicon carbide (SiC) systems will be investigated to reflect the scope and the depth that such an approach can explore.

2. EELS "Spectrum Separation" Approach: Model Si₃N₄ System

The spatially-resolved EELS analysis can provide chemical information from small volumes, especially for light elements that are the major constituents for most ceramic materials. However, even with a nanometer or sub-nanometer



Fig. 2 Schematic of the spatial equivalence to the "spectrum separation" approach.

probe, chemical composition of the amorphous film of ~ 1 nm thick still could not be measured directly. This is because the intensity shape of the fine probe extends typically to several nanometers, and other effects such as beam broadening may add further complication. Meanwhile, EELS analysis, especially when performed in a dedicated scanning transmission electron microscope (STEM, model VG-HB501) attached with a cold field-emission gun, can generate information with an energy resolution better than 1 eV. This tool provides us the possibility to look at details into the EELS spectra, or energy-loss near-edge structures (ELNES), which can yield information on chemical states and chemical bonding. Exploring the ELNES characters for a same element in different environments, the "spectrum separation" approach (Fig. 2) was developed to yield chemical composition and other information of the inter-granular amorphous film in an indirect way.^{10,12,13)}

As shown in Figs. 1 and 2, inter-granular amorphous film in a high purity HIPed Si₃N₄ ceramic provides an ideal model system to demonstrate this approach. It is well studied that amorphous films in this Si₃N₄ has an equilibrium thickness of 1.1 ± 0.1 nm in this model material.^{7-9,15} Conventional AEM analysis detected oxygen segregation to grain boundary, indicating that the inter-granular film is silicate-based but could not tell whether nitrogen is also present. The "spectrum separation" method probes the ELNES for Si- $L_{2,3}$ edge and distinguishes the ELNES patterns of grain and film. This yields separated contributions in the measured ELNES, as illustrated laterally in Fig. 2 in a box mode of measurement configuration in STEM. In another word, this is an unconventional way of spectral processing to remove the unwanted signal from grains unavoidably included in the measurement.

The procedure of spectral processing is demonstrated in Fig. 3. In the actual experiment, not only the spectrum covering the interested film (the so-called "on" spectrum) was recorded, which corresponds to the left-hand side of Fig. 2, another spectrum from the adjacent grains was also taken as the reference (the "off" spectrum). The two parts in the righthand side of Fig. 2 represent two different ELNES patterns for $Si-L_{2,3}$ edge corresponding to the film and to the grains, respectively. The latter ELNES pattern is the same as the off spectrum except a difference in the overal intensity. The on and off $(Si_3N_4 \text{ here})$ patterns are shown as the thick lines on top of Fig. 3. The key here is to subtract right amount of the off spectrum away in the on spectrum. A systematic subtraction is employed to gradually increase the removal factor and to monitor the over-subtraction. A series of subtractions with the amounts of off spectrum increasing in steps of 5% are displayed in Fig. 3, the thick line among them is the one with least mixture of signal from the adjacent grains, which corresponds to the interested amorphous film with an uncertainty less than 5% of the off spectrum. To judge this



Fig. 3 Systematic spectral subtraction procedure for "spectrum separation" approach to gain Si- $L_{2,3}$ ELNES of amorphous film (thick line) in the model Si₃N₄ material. (See text.) The two original on and *off* spectra are display also as thick lines on top.

procedure, features in the *off* pattern that belong uniquely to Si_3N_4 grains have to be specified, as indicated by arrows. These features were used as the indication(s) for oversubtraction when any negative shape and/or sign started to emerge.^{10,12)} The step in the removal factors defines thus the accuracy of "spectrum separation", which is limited by the operator's visual judgment. Nevertheless, the result would not differ substantially if the same ELNES indicators were chosen.

Once the ELNES patterns for the film and the grain were successfully separated, the effect can extend to other edges since the same proportions in the *off* spectrum for all the signals should also be removed. In another word, ELNES "ELNES pattern separation" is equivalent to "spectrum separation". Consequently, the full spectrum with all the involved elements can be achieved for the film, one example is given in Fig. 4. With silicon, nitrogen and oxygen signals



Fig. 4 Separated full spectra for grain and film in the model $\mathrm{Si}_3\mathrm{N}_4$ material.



Fig. 5 Parameters for amorphous films in the model Si_3N_4 material: (a) N:Si ratios, (b) N:O ratios, (c) chemical widths (d_{ch}).



Fig. 6 Correlation of N:Si in amorphous films with: (a) chemical widths, (b) N:O in the model Si₃N₄.

available, chemical composition of the inter-granular amorphous film is ready for quantification. Carbon signals in Fig. 4 come from surface coating for TEM specimen to reduce charging effect. The EELS spectrum for the \sim 1 nm thick inter-granular film clearly displays nitrogen, revealing that the grain boundary layer made of a new oxynitride phase.¹¹

Although the equilibrium thickness for films in the model Si_3N_4 material was observed by HREM, an equilibrium composition was not found by EELS analysis. Chemical compositions of 24 films were measured for in this material. All the N:Si and N:O ratios are plotted in Figs. 5(a) and (b) respectively. Peaked at 0.65 and 0.45 respectively, the range of variation reaches 30% or more in both plots, which are substantially larger than the variation in film thickness and do not support the existence of an equilibrium value. The uncertainty of each spectral subtraction was typically 5–10% as discussed previously, and should not exceed 20% by counting in thickness variation.

As shown in Fig. 2, the separation of EELS spectra is also the separation of the corresponding spaces, leading to an alternative calculation of the thickness for inter-granular film, or chemical width (d_{ch}). This is complementary to the structural width by HREM. It is realized by associating the intensities of separated spectra with the corresponding volumes (different widths) via the respective elemental densities in the following formula:¹³⁾

$$d_{\rm ch} = \frac{w}{1 + \left(\frac{I}{I_{\rm f}} - 1\right)\frac{n_{\rm f}}{n_{\rm g}}} \tag{1}$$

where *w* is the width of probed area, *I* and *I*_f are the total and film intensities in the *on* spectrum, and *n*_f and *n*_g the atomic densities in film and in Si₃N₄, respectively. All are known or measurable except *n*_f, which can be estimated with the help of film composition by using a weighted combination of atomic densities for Si₃N₄ and SiO₂.

The resultant d_{ch} for these measured inter-granular films are given in Fig. 5(c). Their average is about 1.35 nm with variation considerably smaller than for both ratios.¹¹⁾ Although HREM measured the film width as 1.1 nm, the discrepancy can be rationalized by the likelihood that such EELS analysis includes the last crystalline planes from both sides the amorphous film.

In Fig. 6 the compositions and chemical width for each film are presented in a different way. There is no clear correlation of d_{ch} with the film composition as shown in Fig. 6(a). In contrary, N variation to both Si and O exhibit a linear trend in Fig. 6(b). The latter demonstrates good repeatability

of composition measurement as well as the large variation in composition.

3. Variation in Film Width: High Purity Si₃N₄ with Minimal SiO₂

It was widely accepted that there is an equilibrium thickness for amorphous films in a given Si₃N₄. Such equilibrium thickness was also found independent to the amount of SiO₂ between 2.5-17 mass% in the otherwise undoped Si_3N_4 . $\overline{7-9,16,24}$ This is because that the equilibrium thickness is not determined by the remote liquid SiO_2 phase at triple-pockets.^{5,18,19)} However, a Si₃N₄ material with much less SiO₂ impurities (~0.55 mass%) exhibited a narrower thickness of 0.6 nm instead of the common 1.0–1.1 nm.¹⁶⁾ This change has been explained by the small amounts of CaO impurities believed present in the films, which could shrink the film by breaking bonds in the amorphous network.⁸⁾ By employing the "spectrum separation" approach, a strong variation in chemical width was observed in this material and CaO was found not present in the narrow film, indicating a departure from the equilibrium thickness for inter-granular films.¹⁷⁾

The EELS analysis was carried out on three inter-granular films (film 1-3) in this Si_3N_4 sample where the grain size is so large that there were only a few grain boundaries suitable for analysis. Typical EELS spectra for these films were obtained using the "spectrum separation" approach, as given in Fig. 7. From film 1 to 3, N:O ratio changes about three times. This range of variation is comparable to that in the model Si_3N_4 material presented in the previous section.

However, corresponding chemical widths exhibit even strong variation by using formula [1]. Each film was measured repeatedly about 10 times and their chemical widths are plotted as separate histograms in Figs. 8(a), (b) and (c) respectively. Each chemical width has a quite narrow distribution with deviation around 10%, which results no overlapping and indicate good repeatability and reliability. The three films all have different chemical widths: 3.5 nm,



Fig. 7 Processed EELS spectra for 3 films in a Si_3N_4 ceramic with minimal SiO_2 .



Fig. 8 Histograms of chemical widths for 3 films in the $\rm Si_3N_4$ material with minimal SiO_2.

1.4 nm and 0.9 nm. Employing the empirical difference of 0.25–0.3 nm between the structural and chemical widths as experienced in the previous section, the structural widths for these films should be about 3.2 nm, 1.1 nm and 0.6 nm, respectively, if HREM observations were carried on the same films. Nonetheless, the film 3 matches well to the previously observed of equilibrium thickness for the same material,¹⁶ while the film 2 matches to the typical equilibrium thickness in the undoped Si₃N₄ ceramics,¹⁵ leaving the much wider film 1 matches to none.

Despite absence of common character for the three films in either composition or width, there still exists a correlation between the chemical composition and width in this material. As plotted in Fig. 9, nitrogen content in the films decreases monotonically with the increase of the film width. This correlation of composition-width indicates how the amorphous films differ systematically. The average film composition and width for the model Si_3N_4 material is also plotted



Fig. 9 Correlation of chemical width and nitrogen content in 3 films in the Si_3N_4 with minimal SiO₂.

in Fig. 9 as a comparison. Indeed, the film 2 is the same as the equilibrated films in typical Si_3N_4 materials, while the other two films are rather different with the equilibrium films.

The significantly different films in this material may not be because of them not reaching equilibrium, nor be an effect of selective presence of Ca impurities. It is likely that the minimum amount of SiO_2 impurities, which could not fill most of triple-pockets, created different types of intergranular regions. Absence of glassy SiO_2 pocket connected to a grain boundary would increase the attractive capillary force, hence to shrink the film. Widening up of thin film is likely to have other origin.

4. Dopant Saturation in Film: Si₃N₄ Doped with 100 ppm Levels of CaO

The force balance model predicted that the equilibrium film thickness in a given material can be changed by cation additives segregated to grain boundary, which modifies either the attractive Van der Waals force or one of the repulsive forces.^{5,25)} Doping of 100 ppm levels of CaO additives into the high-purity HIPed Si₃N₄ has created an excellent example to show how shifts of force balance changed the equilibrium thickness.⁸⁾ As shown in Fig. 10 (upper panel), the equilibrium film thickness shrinks from the initial 1.0 to 0.7 nm at CaO doping level below 100 ppm but expands with further doping. The Ca cations first break some bonds in the SiO₂ network to weaken the repulsive steric force, and more Ca cations cerate the repulsive electric-double-layer force that thickness the amorphous films gradually from 0.7 to 1.5 nm.

However, quantitative analysis of Ca segregation to grain boundary, measured as excess,^{11,15)} indicates a different scenario. As seen in the lower part of Fig. 10, Ca segregation saturates at 200 ppm level and no further increase was detected, which can not explain the further thickening of the amorphous film from 1.1 nm to 1.5 nm.¹⁵⁾ It is not the levels of Ca segregation but its deviation that has increased. The "spectrum separation" approach was employed to look into



Fig. 10 Trends of structural (upper) and chemical (lower) widths for amorphous films in Si_3N_4 ceramics doped CaO additives.



Fig. 11 Typical processed EELS spectra for amorphous films in CaOdoped Si_3N_4 (from top to bottom): 450 ppm, 220 ppm, 80 ppm.

this discrepancy between the structural and chemical characters induced by CaO doping. Three typical EELS spectra corresponding to the inter-granular films in the three Si_3N_4 materials with different CaO-doping levels are shown in Fig. 11. N:O ratios do not differ significantly between them, while calcium content was very low for the sample with low Ca-doping. This is consistent with the segregation measurement and the films are basically the same in the two samples with high Ca-doping.

To understand wide distributions for Ca segregation, Ca excesses and Ca:O ratios of individual films are plotted sideby-side as histograms for the three samples separately in H. Gu



Fig. 12 Histograms of Ca excess Γ_{Ca} (left panels) and Ca/O ratio (right panels) for amorphous films in CaO-doped Si₃N₄.

Fig. 12. Both histograms for low doping sample display narrow distributions. However, Ca excesses exhibit similar bi-modal distributions in both the high doping samples with populations peaked at around 2 and 3.5 atoms/ nm². Contrarily, Ca/O ratios exhibit mono-modal distributions centered at around 0.08 for both materials. These behaviors suggest that there might be two different types of inter-granular films with similar Ca/O ratios. Two neighboring films with different Ca and O excesses and are labeled in a STEM image in Fig. 13. They belong to different groups in the bimodal distributions. It is indeed that Ca excess differs concurrently with O excess, making Ca/O ratios close to one another. The film with lower Ca and O was straight (flat) and parallel to prism plane of the grain to the left, while the film with more segregants was slightly curved. This behavior was observed repeatedly.¹⁵⁾ It is the difference in grain surface crystallography that dictates the Ca segregation.

It is now possible to explain the discrepancy in structural and chemical behavior for the films in these CaO-doped Si₃N₄ ceramics. CaO segregation at doping level about 200 ppm did saturate in the films, and extra dopants went to the triple pockets.¹⁵⁾ However, the saturation level differs for film parallel or not parallel to prism plane, hence creating bimodal distributions. Indeed, deviations of film width by HREM in these two samples (Fig. 10) are also wide as compared to other two samples, suggesting two equilibrium widths as from chemical analysis. More detailed work is required to further elaborate this picture.



Fig. 13 Two grain boundaries with different amounts of Ca and O in a Si_3N_4 ceramic doped with 220 ppm CaO.

5. Dynamic Change of Amorphous Films: Liquid-Phase Sintered β-SiC Nano-Crystalline Ceramics

Unlike in β -Si₃N₄ where thin amorphous films are present ubiquitously in the microstructure for a variety of additives,²⁶⁾ such films were not present in many β -SiC ceramics. Boron-doped SiC nano-crystalline material is such an example, which exhibited superplasticity without the help of amorphous films.^{21,22,27)} Nevertheless, amorphous films were found in liquid-phase sintered (LPS) β -SiC ceramics, and they did contribute to high temperature deformation by promoting the grain sliding.^{23,28)} These films are not as stable as in Si₃N₄ since they change substantially and may even disappear after deformation at high temperatures.²⁹⁾ A quantitative chemical analysis by the "spectrum separation" approach is the unique way to monitor the physical and chemical changes of these films during the dynamic deformation processes.

LPS SiC ceramics have been deformed extensively at rather high strain rates, either by the tensile or the compressive tests.³⁰⁾ The microstructure of this nano-crystalline material is shown in Fig. 14. Both the small grain size and the presence of amorphous film at grain boundary are two key microstructural factors to favor large amount of deformation. The amorphous films remained after both tensile and compressive deformations in the nano-crystalline material with 7 mass% of Al_2O_3 - Y_2O_3 -CaO as sintering aids. However, the amounts of deformation were moderate since the fracture occurred at relatively shorter times. This is in strong contrast with B-doped nano-crystalline SiC ceramics where the deformation times were 1–2 orders longer.^{23,27)}

By measuring excess of additive segregation before and after the tensile and compressive deformations using EELS,¹¹⁾ changes in the amorphous films can be understood. As shown in Fig. 15, Al excess exhibits a remarkable increase under both deformations, while Ca excess did not change



Fig. 14 Microstructure of a liquid-phase sintered SiC nano-crystalline material.



Fig. 15 Levels of additive segregation to grain boundary versus deformation time in a LPS nano-crystalline SiC material.

much and oxygen excess decreased considerably. The excess data have deviation of 20–30% in each group; their average values are plotted in Fig. 15 against the deformation time. The EELS analysis is not sensitive to detect and quantify Y signal. Nevertheless, the strong increase of Al content and the moderate decrease of oxygen in the films can be explained by a major decrease of Y content in the films. In this case, it is possible to conclude that although survived the deformations, the amorphous films changed from Y_2O_3 -rich composition to Al₂O₃-rich composition. This is well agreeable with formation of YAG phase at triple-grain junctions, which required Y diffusing from the films into the pockets. Such inter-granular diffusion process is correlated to the deformation time, as revealed in Fig. 15.

Typical processed EELS spectra before and after deformation including all the involved elements are shown in Fig. 16. Si and C signals are also present, which may come



Fig. 16 Typical processed EELS spectra of amorphous films before and after deformation in the LPS nano-crystalline SiC material.



Fig. 17 Typical ELNES patterns of Al- $L_{2,3}$ and Si- $L_{2,3}$ edges for amorphous films in LPS nano-crystalline SiC material after deformation. Dashed curve is for SiC grain.

from the buffer layers between the amorphous and the crystalline structures.²²⁾ Y signal is weak and dominated by the carbon signal, preventing its quantification. Comparison of these two spectra confirms the change in Al excess shown in Fig. 15.

More than a tool in the "spectrum separation" approach, ELNES of the film itself can reveal additional information. The Al- $L_{2,3}$ and Si- $L_{2,3}$ ELNES patterns of an amorphous film in the deformed material is given in Fig. 17, together with the Si- $L_{2,3}$ ELNES from a SiC grain to compare the bonding characters. Si- $L_{2,3}$ ELNES for the film does not reveal any character of Si-O bonds.¹⁰⁾ This observation supports the picture of "buffer" layers made by predominantly Si-C bonds.^{22,31)} Al- $L_{2,3}$ ELNES for the film exhibits a doublepeak feature near 80 eV, indicating a co-existence of 4-fold and 6-fold Al-O co-ordinations in the amorphous films, which is a similar situation as in YAG phase presented in the triple pockets.³²⁾

6. Conclusions

By employing the EELS "spectrum separation" approach, $\sim 1 \text{ nm}$ thick inter-granular amorphous films in ceramic materials can be thoroughly characterized. The unique combination of chemical and structural information allows

insightful analysis into the sub-nanometer scale. This paper summarizes a few recent studies on such films in Si-based ceramics. Deviations from the picture of equilibrium film thickness are observed in two Si_3N_4 ceramics, which are rationalized by effect of liquid phase and crystallography. Chemical changes for less stable amorphous films in LPS nano-crystalline SiC ceramics induced by dynamic deformation are also found and quantified, indicating a new way to investigate the driving force for microstructural development.

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