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The Stability of Sapphire in the Presence of Water: an Environmental TEM Study

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The widespread use of sapphire in the electronics industry has been caused by its excellent properties such as high chemical stability, light transmission, thermal conductivity and excellent heat resistance. Moreover, its mechanical endurance (i.e. high strength, high rigidity and high hardness) makes sapphire a highly desirable material for precision mechanical components. In addition, it can be used in applications requiring insulating and microwave-blocking components. Of crucial importance, the production and processing and sapphire can meet large-size and bulk-production requirements demanded by the electronics community. One of the less desirable properties of sapphire and transition alumina is their high affinity to water. While hydration or hydroxylation of alumina may lead to enhanced catalytic activity, it can also lead to the degradation of material properties such as chemical stability. Particularly, surface reactivity and stability is highly dependent on surface termination and stoichiometry, as dictated by hydration and hydroxylation level.[1] This can lead to batch-to-batch variability and performance degradation. In addition to this, the use of energetic particle irradiation may lead to changes in the properties exhibited by sapphire. The electrical degradation of sapphire has been reported upon e-beam irradiation.[2] Others has reported the formation of holes and slots of sapphire and other phases of alumina.[3-5] Furthermore, the reactivity of water radiolysis products from energetic particle bombardment can also result in the degradation of alumina surfaces.[6] Hence, it is imperative to understand the role of water in the reactivity and microstructural modification of sapphire.

We herein explore the reactivity of sapphire to water and e-beam irradiation by means of environmental transmission electron microscopy (ETEM). This was achieved using an accelerating voltage of 80kV and a water vapor pressure of 10^{-5}, 10^{-1} and10^{0} Torr. The reactivity and microstructural evolution of sapphire was studied via TEM micrographs, Fast Fourier Transforms (FFT) and Electron Energy Loss Spectroscopy (EELS) at various water levels. The e-beam was focused to fixed areas, time and doses to explore the role of the various levels of water on the microstructure of the sapphire. Pore formation is evident on irradiated areas at the water levels explored. At low water level, a large degree of damage is observed (Figure 1). This is ascribed to the dissociation and desorption of oxygen as proposed by the Knotek-Feibelman core-hole Auger decay model.[7] Within the regime of low water vapor levels, increased damage is ascribed to reduced scattering and decrease in recombination of radiolysis-species in the microscope.[8] Interestingly, the most drastic change in microstructural evolution occurs above a water level threshold of 10^{0} Torr. At this water level, significant swelling, reconstruction and large pore formation (swizz-cheese like) is evident (Figure 2). EELS spectra were acquired for samples irradiated using short and prolonged e-beam exposures. These studies were used to examine the reactivity of sapphire to water and determine the stability of the surface. The presence of hydroxyl groups was clearly observed for regions sampled with short e-beam exposures.[9] These hydroxyl groups demonstrated to be very volatile to e-beam irradiation and their disappearance was evident at prolonged exposures. The volatility of surface hydroxyl was accompanied by the creation of vacancies and defects for longer exposures. The appearance of a shoulder in the EELS spectra depicting the formation of vacancy sites is consistent with pore formation observed upon swelling and reconstruction of sapphire at higher water levels. These are a set of preliminary results for a series of in-situ surface reactivity studies on sapphire.

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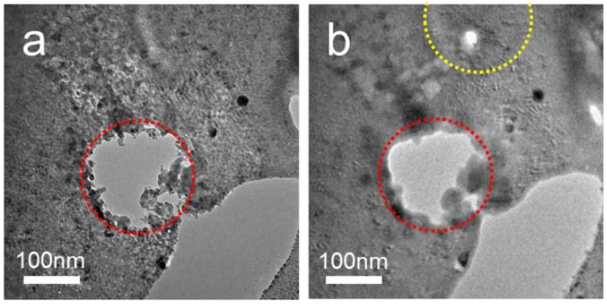

Figure 1. Microstructural evolution of sapphire irradiated under various water vapor conditions. (a) Red dashed circle shows an irradiated area using 10^{-5} Torr of water vapor, with a large degree of damage. (b) Yellow dashed semi-circle shows an irradiated area using 10^{0} Torr of water vapor, with a smaller degree of damage. Swelling of the area irradiated with 10^{-5} (red dashed circle) is also evident.

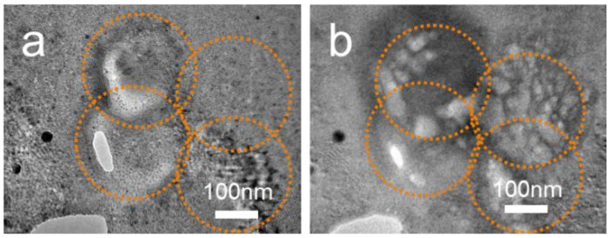

Figure 2. Microstructural evolution of sapphire irradiated using 10^{-1} Torr of water vapor (a), then exposed to 10^{0} Torr of water vapor (b) in the absence of e-beam bombardment. Swelling, reconstruction and void formation is evident at irradiated areas after 10^{0} Torr of water vapor (compare orange dashed circles in a & b).