SURFACE STRUCTURE FORMATION OF PRESOLAR ALUMINA (Al_2O_3): HYDROGEN AND HELIUM ION IRRADIATION EXPERIMENTS. A. Takigawa[1, 2], T. Matsumoto[3], A. Miyake[2], A. Tsuchiyama[2], Y. Nakata[4], and K. Yasuda[4] [1]Department of Terrestrial Magnetism, Carnegie Institution of Washington, Washington, DC 20015, USA. E-mail: atakigawa@ciw.edu. [2]Department of Geology and Mineralogy, Kyoto University, Kyoto, Japan, [3]Department of Earth and Space Science, Osaka University, Toyonaka, Japan, Department of Research and Development, [4]The Wakasa Wan Energy Research Center (WERC), Tsuruga, Japan

Introduction: Corundum, which is the thermodynamically stable crystal phase of alumina (Al_2O_3), is one of the first condensates from the gas of the solar composition [1]. Hundreds of presolar alumina grains discovered in primitive chondrites [e.g., 2] might have condensed in outflows from evolved stars and been incorporated into the molecular cloud where the solar system has formed. We previously showed that many presolar alumina grains have irregular and rough surface structures [3]. We have also indicated that such surface structures have not formed during acid treatments to isolate alumina from a chondrite by dissolution experiments of alumina polymorphs including corundum and amorphous alumina.

Comparison between infrared observations of evolved stars and interstellar medium (ISM) have shown that the abundance of crystalline silicates around evolved stars is much higher than that in the ISM [4]. One possible explanation for this discrepancy is amorphization of crystalline silicates in the diffuse ISM by interaction between dust and low energy (<1MeV) cosmic rays or light ions accelerated by shockwaves from SNe [5]. Several irradiation experiments have been performed and shown that irradiation of a few to tens KeV H^+ and He^+ ions can effectively cause amorphization of olivine and enstatite [6-8]. Irradiation of He^+ or H^+ ions forms bubbles inside the target material and a high dose irradiation deforms surface structures of the target observed on silicates as orange skins [6-8] or blisters [9].

If ion irradiation is responsible for amorphization of crystalline silicates in the ISM, alumina grains formed around evolved stars should also be irradiated with such low energy cosmic rays or ionized gas in supernova shocks. Moreover, presolar grains in the early solar system have also been irradiated with a strong solar wind from the early Sun. As a possible cause of rough surface structures of presolar alumina grains, we carried out irradiation experiments of H_2^+ and He^+ ions to alumina targets and investigate their structural changes and surface deformation.

Experiments: Irradiation experiments have been peformed in an ion-implanter using a microwave ion source (Hitachi) at The Wakasa Wan Energy Research Center. Wafers of single crystal corundum and ~1μm sized grains of several alumina polymorphs were used as targets for irradiation. Corundum wafers with largest planes of {0001}, {11-20}, and {10-10} (Dalian Keri Opt. Tech. Co. Ltd.) were cut into chips of 2-3 x 10 x 0.5 mm in size. Both-sides of the wafers had been chemically polished. A {0001}-oriented wafer was used as a target in each of all experiments, and {11-20}- and {10-10}-oriented wafers were also used in some experiments to examine the anisotropy of irradiation damage. Alumina grains with α-, δ-, γ-, and χ-alumina structures produced by dehydration of aluminum hydroxides, and amorphous alumina grains produced by the sol-gel method were dispersed onto a Cu plate separately. The corundum wafers and copper plates with alumina grains were fixed with a stainless frame on a copper holder together.

The target holder was put in the chamber and evacuated to ~10^{-4} Pa before ion irradiation. In this study, target samples were irradiated with 50 keV He^+ ions and with 10, 20, and 40keV H_2^+ ions, which are equivalent to the H^+ ions with energy of 5, 10, and 20keV, respectively. Irradiation doses were 10^{16}, 10^{17}, and 10^{18} ions/cm^2. During irradiation, the beam current density was kept at ~10 μA/cm^2 and the temperature of the sample holders were kept at ~30°C by water-cooling.

The irradiated surfaces of the corundum wafers were observed with field-emission secondary electron microprobe (FE-SEM, JSM 7001F). An ultrathin section was extracted from the {11-20}-oriented wafer irradiated with 40keV H_2^+ ions with a dose of 10^{18} ions/cm^2 using focused ion beam (FIB, FEI Quanta 200 3DS) and analyzed with transmission electron microprobe (TEM, HITACHI H8000K).

Results: Blister structures were observed uniformly on surfaces of the corundum wafers irradiated with 40keV H_2^+ ions with a dose of 10^{18} ions/cm^2 (Fig. 1), while no clear surface structure was observed on the wafers irradiated with doses of less than 10^{17} ions/cm^2. Blistering has not occurred on corundum surfaces by irradiation of <20 keV H_2^+ ions with doses of 10^{16}, 10^{17}, and 10^{18} ions/cm^2. Similar blisters were also observed on the wafers irradiated by 50keV He^+ ions with a dose of 10^{18} ions/cm^2, while no blister was confirmed on the surfaces irradiated 50keV He^+ ions with doses of 10^{17} and 10^{16} ions/cm^2. Size and density of blisters, and threshold energy of blistering did not depend on the orientation of corundum surfaces.

An FIB ultrathin section across a blister formed on a {11-20}-oriented corundum wafer is shown in Fig. 2. The thickness of the blister skin was 170-220 nm. The diffraction pattern obtained from the right part of the blister skin shown in Fig. 2 was identical to the pattern of corundum obtained from the non-irradiated region. The diffraction spots from the blister slightly split and the dark-field image formed using the split spots indicated that the left part of the blister skin in Fig. 2 had been plastically deformed.

We compare the SE images of α-alumina grains before and after irradiation with 40 keV H_2^+ with a dose of 10^{18} ions/cm^2 (Fig. 3). No blistering or clear surface deformation was observed on the grain surface, although this grain was irradiated simultaneously with the corundum wafers shown in Fig. 2. Little differences were also confirmed on particles of alumina polymorphs other than α-alumina and on the alumina grains irradiated at the other experimental conditions of this study (20-40 keV H_2^+ and 50keV He^+).

Discussion: We simulated implantation of 20 keV H^+ ions into Al_2O_3 using SRIM 2013 [10]. Vacancies are created by collisions between an implanted ion and a target atom or between a recoiled and a target atom. The density of vacancies is 0.007 even at the depth of the maximum vacancy density (150 nm from the surface), which could explain the diffraction pattern of corundum from the blister skin. The depth that the distribution of implanted H^+ ions has a peak (170 nm) corresponds to the thickness of the blister skin (Fig. 2).

The typical size of blisters observed on the corundum surfaces irradiated by 40 keV H_2^+ with a dose of 10^{18} ions/cm^2 is 3-5 micrometers, which are larger than the irradiated particles (e.g., Fig. 3). The blisters may form by coalescing small bubbles of hydrogen or helium gas at the damage depth of maximum vacancy [9] and the gas molecules that formed blisters should be come from a larger area than the size of blister. Moreover, some of the irradiated ions would have penetrated the target grains because edges of rounded grains and some parts of grains are thinner than the depth of the maximum implanted ion density of 170 nm. Therefore the total amount of ions implanted into a small grain would be insufficient to form a blister.

Irradiation experiments in this study showed that irradiation of 10-20 keV H^+ and 50 keV ions may not be directly responsible for the formation of the rough surface structures observed on the presolar alumina grains [3] but formation of bubbles and increase of vacancies could affect solubility of alumina in acid solutions or weaken the strong α-alumina structure. Further dissolution experiments of irradiated alumina grains will be performed to reveal the origin of the surface structures of presolar and solar alumina, which might be a clue to understand the processes that presolar alumina grains have experienced in the ISM and early solar system.

References: [1] Wood J. A. and Hashimoto A. (1993) *GCA*, 57, 3277. [2] Nittler L. R. et al. (1997) *ApJ*, 483, 475. [3] Takigawa A. et al. (2011), *LPS XXXXII*, #2599. [4] Kemper F. et al. (2005), ApJ, 633, 534 [5] Jones A. P. et al. (1994), *ApJ*, 433, 797. [6] Demyk L. et al. (2001), *A&A*, 368, L38 [7] Carrez P. et al. (2002) *MAPS*, 37, 1599. [8] Jäger C. et al. (2003), *A&A*, 401, 57. [9] Muto S. and Enomoto N. (2005), *Material Transactions*, 46, 2117. [10] Ziegler J. F. 2013, *The Stopping Range of Ions in Matter*, ver.2013, http://www.srim.org

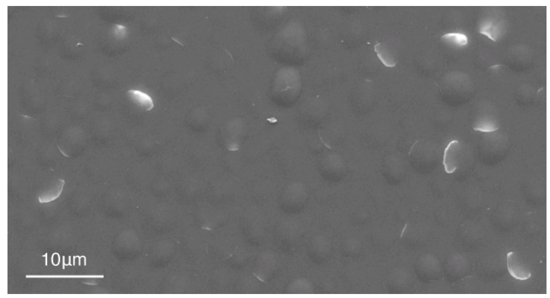

Fig.1 Surface of the {11-20} corundum wafer irradiated with 40keV H_2^+ ions (10^{18} ions/cm^2).

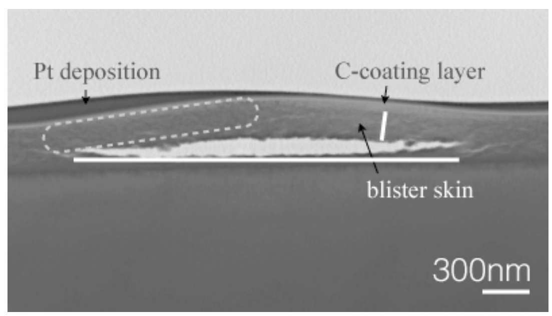

Fig. 2 FIB lift-up section of a blister on the {11-20}-oriented corundum wafer irradiated with 40 keV H_2^+ ions (10^{18} ions/cm^2). The crystal orientation of the area indicated by a dashed circle is slightly different from the other region.

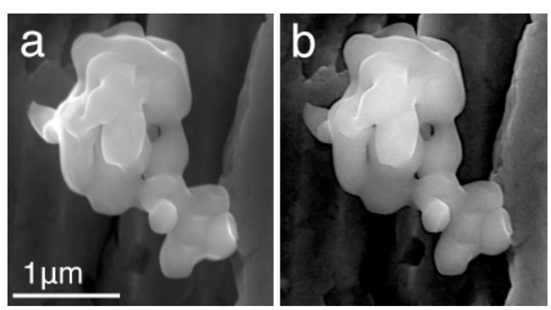

Fig. 3 Corundum (α-Al_2O_3) grains (a) before and (b) after irradiation of 40 keV H_2^+ (10^{18} ions/cm^2).