LABORATORY EXPERIMENTS ON THE FORMATION OF PAH CLUSTERS AND THEIR ALTERATION WITH INORGANIC MATTER BY PLASMA, ULTRAVIOLET AND ELECTRON BEAM IRRADIATION. M. Saito, Y. Kimura, and C. Kaito, Laboratory for Nano-Structure Science, Department of Physics, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu-shi, Shiga, 525-8577, Japan. rp010027@se.ritsumei.ac.jp, ykimura@se.ritsumei.ac.jp, kaito@se.ritsumei.ac.jp

Introduction: Polycyclic aromatic hydrocarbons (PAHs) have been considered most plausible candidates of the unidentified infrared bands observed from various astronomical objects including young stars [1,2]. PAHs consist of carbon atoms arranged in benzene rings terminated by hydrogen atoms. They have C-C and C-H bonds, which show the vibration modes at mid-infrared region. In order to elucidate the behavior of the PAHs in the early Solar Nebula, I have performed experimental studies on the formation of PAH clusters with and without inorganic elements, alteration by ultraviolet irradiation and plasma field, and measured their infrared spectra in the laboratory. If the mechanisms of formation and growth of PAH clusters via experimental studies were elucidated, it will be able to discuss the behaviors of PAH clusters including interaction with inorganic grains in the early Solar Nebula. Indeed, recently, it has been reported the crystallization temperature of the amorphous Mg-bearing silicate grains is decrease to 300 K from thermal annealing crystallization temperature at ~1000 K, when the amorphous silicate grains have an amorphous carbonaceous layer [3]. Generally, it has been considered that amorphous silicates gradually crystallize via thermal annealing in the hot inner solar nebula over time and then were transported outward and incorporated in comets [e.g. 4,5]. Using this thermal annealing model, the chronology and formation age of comets in the early Solar System has been discussed based on laboratory experiments [6]. The experimental results imply that the crystallization of cometary silicates has been occurred in the coma of comets at each time comet approach the Sun, i.e., not 4.5 billion years ago. As a result, it can be explain how cometary silicate crystallize yet still preserve volatile interstellar ices in their parent comets. Thus, organic materials will strongly affect to the behavior of inorganic materials. The abundances of oxygen, nitrogen and carbon are more than 10 times of that of silicon, magnesium and iron. Indeed, as a result of recent observation, the presence of significant amount of organic materials in the primitive solar nebula has been found. Since we assume that the organic materials affect to the nucleation, growth and crystallization of inorganic cosmic dust, the behavior of organic materials and interaction to the inorganic materials such as silicates, oxides and carbides in primitive solar nebula should be consid-
ered. In the present study, laboratory experiments of nucleation and growth of Si in PAHs gas atmosphere will be also shown. Si interacts with both oxygen and carbon and become a component of many kinds of minerals. In addition, PAHs are widely presented in the universe. Therefore, experiment using Si and PAHs were performed, initially. In the primitive solar nebula, dust particles would be undergone plasma environments and irradiation of cosmic ray during formation and growth. Therefore, growth of PAHs with or without Si in a plasma field and irradiation of ultraviolet or electron beam to the grown particles are also shown.

Experiment: Pyrene and coronene were used as the materials of PAHs clusters. The structures of both PAHs have been shown in Fig. 1. They have a molecular structure constructed by four and seven benzene rings in compact, respectively. Pyrene has two duo C-H bonds and two trio C-H bonds, and coronene has six duo C-H bonds. C-H out-of-plane deformation mode make bands in 11-15 μm region depending on the number of directly adjacent H atoms, because of the coupling between the vibrating H atoms bonded to neighboring C atoms on a ring. PAH clusters were produced by evaporation of commercial powder in He gas of 80 Torr using an experimental setup as shown in Fig. 2. Commercial PAH (pyrene or coronene) and Si powders were charged on upper and lower tantalum boats. A boat with Si was electrically heated at about 2000 K. Then, the other boat with a PAH was heated by the convection of He gas. As a result, PAH was simultaneously evaporated with Si. In the case of the experiment in Fig. 2(a), Si should be condensed and growth in the PAH vapor, because the sublimation temperature of PAHs are quite lower compared with Si. In the case of the experiment in Fig. 2(b), Si particles could be produced before it contact with PAH vapor. Therefore, sublimated PAH molecules may condense on the Si particles in addition to the homogeneous nucleation, when Si smoke particles were cooled below the sublimation temperature of the PAH. These experiments are supposed reprocessing of original interstellar materials in the solar nebula. The produced clusters collected on a glass plate placed 8 cm above the upper boat for measurements of infrared spectra and on a standard Cu transmission electron microscope (TEM) grid supported with amorphous...
carbon film for observation of the size and the structure of the grains.

**Initial Results:** Figure 3 shows mid-infrared spectra of (a) Si-coronene, which is corresponding to Fig. 2(a), (b) coronene-Si, which is corresponding with Fig. 2(b) and (c) coronene without Si. In the spectrum (b), a significant feature at 9 μm can be seen in addition to the sharp peaks at 7.6, 11.8 and 18 μm attributed to coronene. The 9 μm feature is caused by the asymmetric stretching vibration mode of Si-O. The appearance of the feature at 9 μm shows production of SiO particles. Namely, although Si particles were produced and passed in the vapor of sublimated coronene, the deposition of coronene on the pre-nucleated Si particles may be insufficient or not occurred. As a result, Si surface was oxidized by taking out the specimen into air. In the case of the experiment in Fig. 2 (a), since Si is grown in the coronene vapor, Si may incorporate in the coronene clusters. Therefore, there is no chance to form SiO. As a result, 9 μm feature does not appear in the spectrum in Fig. 3(a). Since the 11-12 μm feature by silicon carbide did not show up in the both spectra, Si does not react with coronene molecules, even if Si is nucleated and growth in coronene vapor. Slight difference of the feature of coronene is visible in the spectra. The intensity of a characteristic double peak at 11.8 μm caused by duo of C-H vibration mode is changing by the existence of Si.

Although ultraviolet at 254 or 365 nm was irradiated to the samples of coronene and pyrene with Si, which were produced by the method of Fig. 2(a), the infrared spectra did not change for the duration of 15 hours, which is corresponding to the total flux of $4.3 \times 10^{21}$ and $7.5 \times 10^{21}$ photons/cm$^2$, respectively. On the other hand, when electron beam of 300 KeV for $10^{-3}-10^{-2}$ A/cm$^2$ was irradiated to the samples of pyrene with Si, which was produced by the method in Fig. 2(a), formation of silicon carbide nanoparticles were appeared after about 15 minutes during TEM observation. We will show further experiments including experiments of formation in a plasma field and discussion on the expanding to the environment in the early Solar Nebula on the poster.