

Structural Transformation in Tetrahedral Amorphous Carbon  
induced by Electronic Excitations  
(電子励起によるアモルファスカーボンの構造変化)

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In the progress of nano-technology, manipulation of atoms and molecules in the scale of really nanometers or even atomic sizes has become an important issue. For such atomic manipulations, the use of electronic excitations may provide an efficient approach. That desorption of atoms and molecules from solid surfaces by electron beam irradiation (electron-stimulated desorption =ESD) and that by light illumination (photo-stimulated desorption =PSD) are well known phenomena. Such manipulation is interpretable in terms of adiabatic potential surfaces which generally differ in different electron states: The instability of atoms in the excited states, cause displacements towards new stable positions along the adiabatic potential surface in order to lower the total potential energy. In some cases, the atom configuration, even though it is structurally stable in the electron ground state, disrupts or substantially alters while the electron (electrons) is (are) in the excited state.

Usually in solids, however, the lifetime of electronic excitation states is generally short, because before inducing atomic displacements, the electronic excitation states are rapidly dissipated to other freedoms, such as photons (fluorescence), other electrons (Auger process), another electron excitation state (resonant transfer), etc, through many paths that are absent in isolated molecules. For this reason, electron-stimulated atomic displacements are usually uneasy in solids comparing with that in isolated molecules. In this respect, carbon is an exception: Carbon is a light element and therefore its movement can be accelerated more quickly than heavier elements. Also carbon has high potential to condense to various thermally stable structures. Hence, for carbon materials, it has been expected that the solid structure can be changed as a result of electronic excitations.

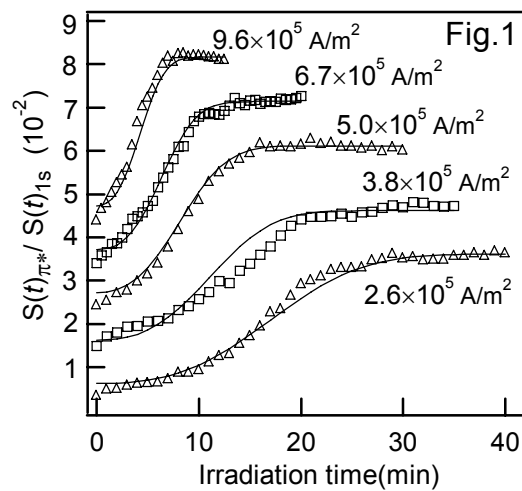
In fact, our group found that a restructuring of ta-C (tetrahedral ( $sp^3$  bonding atoms being more than 80%) amorphous carbon) films is induced by irradiation of 200keV electron beam in transmission electron microscope (TEM). There are newly formed short-range ordered structures by examining the TEM images and by analysis of diffraction patterns. This phenomenon was proved to be a structural transformation from  $sp^3$  to  $sp^2$  configurations by EELS (electron energy loss spectrum) measurement.

The salient feature of carbon solids, the quite structure-sensitive physical properties, arouses our interest in the applications of the electronic excitations to fabricate some solid structures, peculiarly with the properties that could not be achieved otherwise, such as high efficient negative emission effect. This motivated us to study the microscopic mechanism of such effects of electronic excitations, especially how electronic excitation states are responsible for the restructuring in carbon solids. In the case of electron irradiation, however, different excitations are induced depending on the electron beam energy, phonon excitation, valence electron excitations (plasma

excitations), core electron excitations, displacement damage, secondary electron emissions, and so on. Therefore, controlled excitations are highly necessary for the microscopic mechanism to be elucidated.

This dissertation consists of five sections. The section 1 is for the introduction of the present study. The section 2 is devoted to provide the readers with basic knowledge about the concept often used in the literature and the theories related to the effects investigated in the present study. The sections 3 and 4 present the main originality of the present dissertation. Section 3 concerns a systematic study of the  $sp^3$  to  $sp^2$  structural conversion in ta-C films induced by TEM electron beam irradiation, and Section 4 describes a newly found similar effect induced by soft X-ray illumination that excites carbon core electrons. The summarization of present study in Section 5 added with some comments for problems that remain for future study.

For the electron-irradiation-induced effect, using JEM-2010F (JEOL) equipped with a filed emission gun and a parallel EELS spectrometer (Gatan), it's been systematical measurements of the temporal evolution of the  $\pi^*$  peak in EELS core loss spectra, which representing graphite structure. The kinetics of the  $sp^3$  to  $sp^2$  structural conversion in ta-C films induced by TEM electron beam irradiation, was analyzed in the framework of the Johnson-Mehl-Avrami model, with the carefully consideration of the non-uniform profile of the electron beam used for intense irradiation. As shown in Fig. 1, the theoretical curves(lines)



are of fitting with the experimental data(marks), calculated for various combinations of adjustable parameters, which denoting the growth dimension and the beam intensity dependence. It shows that the expanding velocity of the new phase front increases in proportion to the irradiation beam current density, proving an experimental support for the notion that the effect is possibly caused by electronic excitation effect. It is also to be concluded that the growth proceeds is in three dimensions from preexisting nuclei.

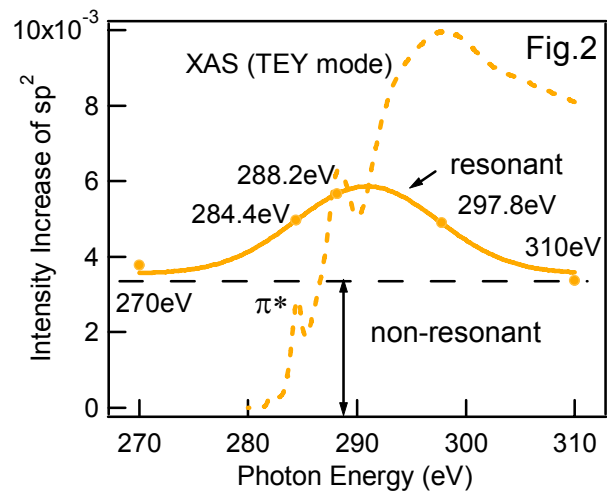
Generally, for such atomic rearrangement to occur in an extended scale, atomic diffusion must take place to some extent. Here arose a question whether or not the enhanced process is the atomic diffusion. Then, the measurement of the increase of  $\pi^*$  peak in EELS spectra with elapsed time  $t$  of annealing at various temperatures for the sample films, has been conducted under a condition that the irradiation with the same electron beam current density. In this measurement, the samples had been first subject to heating at the maximum temperature so that the annealing should start isostructurally. By assuming the expanding velocity  $v$  of the phase front to be proportional to  $\exp(-Q/k_B T)$ , and considering that the experimental data should be scaled in one unit of  $v \times t$ , which should be unified to a master curve, there is an Arrhenius plot of  $v(T)$  vs  $1/T$ . Based on the

measurement result that activation energy  $Q$  is as small as  $\sim 0.03\text{eV}$ , it indicates a dissociative diffusion mechanism that is triggered by electron irradiation: Carbon atoms in the stable positions are displaced by electronic excitations or electron knock-on impacts to meta-stable sites, from which the atoms diffuse thermally with the very low migration energy.

In order to avoid possible effects of electron knock-on impacts, which would not occur by soft X-ray illumination, the experiment of soft X-ray illumination in ta-C films has been performed, with selective incident photon energies. The effects of soft X-ray illumination in ta-C films was expected from previous experiments by Ma et al. on diamond crystals and those by Harada et al on HOPG (highly oriented pyrolytic graphite) which both have shown a large atomic displacement during the very short lifetime of core excitons generated by resonant excitations of carbon 1s core electrons. Several theoretical calculations also showed that the  $sp^3$  carbon-carbon bonding becomes unstable in the core exciton state.

Intense soft X-ray illumination experiments have been done in BL27SU, undulator beam line at Spring-8 equipped with a flat field soft X-ray spectrometer. We illuminated the ta-C film samples with nearly monochromatic soft X-rays (FWHM=7 eV) in various photon energies ranging near the  $C_{1s}$  core edge. The illumination power, of the order of  $10^{18}$  photons/s $\cdot$ cm $^2$  in the intensity, was adjusted to equalize the total electron yield of the sample, so that possible effects of secondary electrons were made even. It was measured *in-situ* spectra of X-ray absorption (XAS), to detect a structural change that occurred between before and after the illumination. The XAS spectra were acquired in total electron yield (TEY) mode and fluorescence (FL) mode for surface-sensitive and bulk-sensitive measurements, respectively.

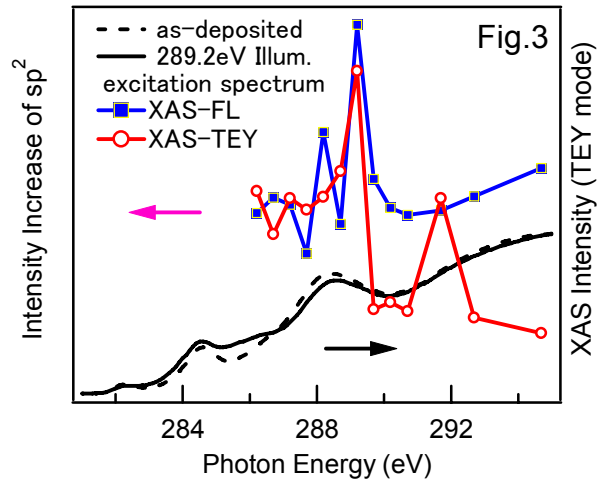
As shown in Fig. 2, after soft X-ray illumination, graphitization took place with the increase of  $\pi^*$  peak in XAS-TEY spectra. By varying the soft X-ray photon energy for illumination, it is able to measure the excitation spectrum of the total structural change effect vs photon energy. The result indicated that the increase of  $\pi^*$  peak intensity has two components, a resonant component peaking around the characteristic



core excitation absorption peak of ta-C films (288eV), and a non-resonant increase component independent of the photon energy used for the illumination. A careful examination of the change in the XAS-spectra for various illumination energies revealed that the structural change induced by the resonant excitation is characterized by the increase of 284.5eV XAS peak representing graphitic order, while the change induced by the non-resonant excitation is by the increase of spectral intensity around the 283.5eV and 285.5eV XAS peaks. In bulk-sensitive XAS-FL spectra, a more dramatic increase in 283.5eV XAS peak was evident and a blue shift of the characteristic core

absorption peak of ta-C films was induced. Since 283.5eV peak is attributed to disordered structures or dangling bonds in graphite, these facts suggest disordering effects of non-resonant excitations.

More detailed measurements of the excitation spectrum of the energies around the characteristic core excitation peak of ta-C films, showed a resonant increase of XAS intensity around  $\pi^*$  peak in XAS-TEY and XAS-FL when the sample was illuminated with 289.2eV soft X-ray (Fig. 3). The fact that the excitation spectrum has a peak near the 288 eV, which is characteristic core excitation absorption peak of ta-C films, clearly indicates that the resonant structural change is induced by the core excitation.



Although the origin of the 288 eV peak in XAS is not known at present, some literature claims that it originates in core excitons as we had expected. However, the resonant soft X-ray emission spectra excited by 289.2eV photons did not exhibit hot-luminescence, which would be direct evidence for the core exciton mechanism. Other literature claims a similar XAS peak induced by the interlayer states in graphite, possibly originates that the characteristic core excitation peak of ta-C films. If this interpretation is correct, one may have to devise a different mechanism not considered before. Two-hole-states induced by a resonant Auger process might instabilize the structures, however the resonant Auger emission spectra excited by photon energies around the characteristic core excitation absorption peak of ta-C films shows no resonant increase of Auger signal. One more possibility from the resonant Auger emission spectra is the characteristic core excitation peak of ta-C films is explanatively compounded with  $sp^3$ - $sp^2$ , which is not well understood.

In summary, It has been studied the structural transformation from  $sp^3$  to  $sp^2$  configuration in ta-C films induced by electron beam irradiation and soft X-ray illumination. Kinetic analysis of phase growth clearly showed that the phase front velocity increases in proportion to the irradiation beam current density. There is a proposed model that once carbon atoms are displaced by electrons (by electron excitation or by knock-on impacts) to meta-stable positions, they diffuse very rapidly but thermally with low migration energy until they reach graphitic phase boundaries. The similar effects of soft X-ray illumination was found, too, which should not cause knock-on damage at the same time. The effect is a dramatic resonant increase around  $\pi^*$  peak in XAS spectra by intense illumination of the sample with 289.2eV soft X-rays, close to a characteristic core excitation absorption peak of ta-C films. It is also found non-resonant increase of unknown structures independent of the soft X-ray photon energies for illumination.