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Electric Properties in Biofilms Studied by Resonant Auger Electron Spectroscopy

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1. Introduction

Thin films of biomolecules on solid surfaces have attracted much attention in the development of molecular electronics. Among biomolecules, there has been great interest in the nature of DNA's as well as nucleotides on semiconductor surfaces because of their potential applications to nanotechnology such as DNA tips and DNA computers. One of the fundamental problems to be solved is the information about the electric property of DNA thin films deposited on solid surfaces. There have been many works concerning the electric conductivity in DNA films, but the reported results are diverse in a wide range from insulator to metallic [1]. Although the average conductivity in a DNA film can be measured by general four-probe method, the intrinsic conductivity in the direction of one-dimensional strand is unclear due to the difficulty in directly attaching the electrodes at a single molecule.

Resonant Auger electron spectroscopy as well as resonant photoemission spectroscopy is one of the suitable methods to characterize not only electronic structures but also electric properties in a specific site. It has been reported that the resonant photoemission spectra for DNA at the nitrogen *K*-edge photoexcitation shows that the charge hopping model is pertinent for the electric conduction in a DNA duplex [2]. Since the nitrogen atoms are only included in the bases, not in molecular backbones, it is also important to elucidate the charge transport mechanism along the molecular skeleton.

In the present paper, we report on the resonant Auger decay spectra for ATP and DNA molecules following the phosphorus *K*-edge photoexcitation in order to elucidate the charge transfer mechanism along one-dimensional chain in sugar/phosphate energy backbone.

2. Experiment

The experiments were performed at the BL-27A station of the Photon Factory in the High Energy Accelerator Research Organization (KEK-PF). ATP molecules were deposited on highly oriented pyrolytic graphite (HOPG) by vacuum evaporation. DNA molecules were embedded on a surface of an indium plate. The X-ray absorption spectra were measured by plotting a sample drain current as a function of photon energy. Auger electron spectra were measured with a hemispherical electron energy analyzer.

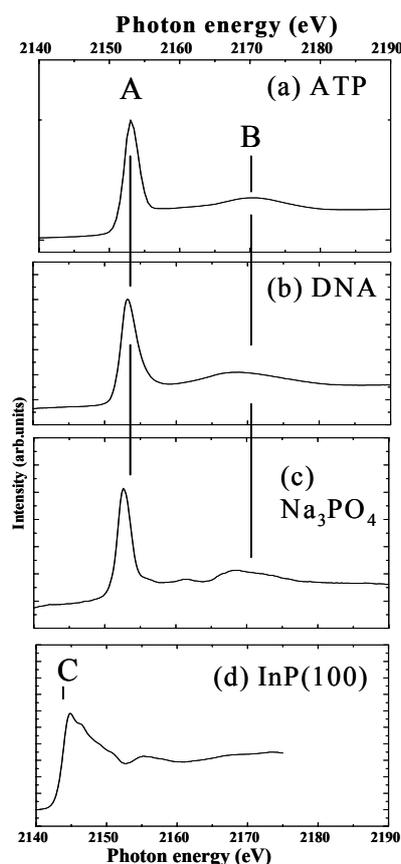


Fig.1 X-ray absorption spectra of phosphorus compounds.

3. Results and discussion

Figure 1 shows the phosphorus *K*-edge X-ray absorption spectra for ATP and DNA together with some reference spectra. For ATP, DNA and sodium phosphate, sharp peaks (marked A) are seen at 2153 eV and broad structures (marked B) are observed around 2172 eV. The peak A is due to the resonant excitation from the P 1s to 3p-derived orbitals (t_2^*) and the higher-energy peak B is originating from shape resonance into the orbitals with d-character.

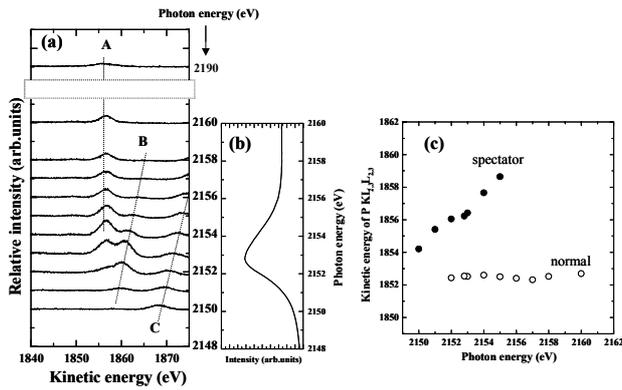


Fig.2 (a) Phosphorus KLL resonant Auger decay spectra for DNA molecule. Peak A with constant kinetic energy is due to normal Auger decay, and peak B is originating from spectator Auger decay. Peak C is due to the C 1s photoelectrons. (b) X-ray absorption spectra around the phosphorus K -edge for DNA molecule. (c) Kinetic energies of P $KL_{2,3}L_{2,3}$ Auger peak as a function of the photon energy.

Phosphorus $KL_{2,3}L_{2,3}$ resonant Auger decay spectra for DNA following phosphorus K -edge excitation are displayed in fig. 2(a) together with the X-ray absorption spectrum (fig.2(b)). For higher energy excitation above the ionization threshold, the P $KL_{2,3}L_{2,3}$ Auger peaks with constant kinetic energy (marked A) are observed. These peaks are due to the normal Auger decays following the ionization of P 1s electrons. For the resonance excitation around 2153 eV, the Auger peak splits into two components. The lower energy component marked A is apparently due to the normal Auger decay. The higher energy one marked B appears only around the resonance excitation energy ($h\nu=2153$ eV). The intensity of the component B is nearly proportional to the X-ray absorption intensity. It has been elucidated that the Auger peaks for insulator are split into two components; spectator and normal Auger peaks, while for metals and semiconductors only one Auger peak is observed [3]. In a spectator Auger process, a core electron is resonantly excited into a valence unoccupied orbital and another electron drops into the core hole, and then the other electron is emitted as an Auger electron. In the case of metals and semiconductors, the time scale of the delocalization of the excited electrons are fast in comparison with the Auger electron emission due to the screening effect of the conduction electrons in the Fermi level. This is the reason why only single Auger peak is observed at the resonant excitation. We confirmed this property in the resonant Auger spectra for InP with semi-conducting property. The energy splitting of the resonant Auger peak in insulator is due to the localization of excited electrons in valence unoccupied orbitals during the Auger decay. Clear peak splitting in Fig. 2 suggests that the DNA molecules have insulating properties around the phosphate backbones.

Another outstanding phenomenon seen in fig 2 is the

energy shift of spectator Auger peaks. In figure 2(c), the kinetic energy of the Auger peaks are plotted as a function of the incident photon energy. In contrast to the normal Auger peaks with constant kinetic energy, the energy of the spectator Auger peaks shift linearly with the photon energy. The energy difference between normal and spectator Auger peaks comes up to 6.5 eV at $h\nu=2155$ eV. The kinetic energy shift of spectator Auger electrons has been interpreted in terms of the Auger resonant Raman scattering [3]. In Auger resonant Raman scattering process, the energy of the incident photon is coherently transferred to the kinetic energy of the Auger electrons. The energy of the incident photon corresponds to the energy difference between the core level and valence conduction band. This means that the linear kinetic-energy dispersion of spectator Auger peaks is observed in wide energy range in insulating solid compared with semiconductor or metal. The degree of the localization of the excited electrons can be estimated from the energy shift of the spectator Auger peaks. Actually, it was reported that the energy widths over which the dispersions in resonant Auger peaks are observed are a measure of the localization of electrons in empty states [4]. The present Auger decay spectra show that the degree of the localization of excited electrons in the valence unoccupied orbitals in phosphate backbone is similar to those for insulating solid with wide gap. The present data reveal that the DNA molecules are wide band-gap insulator in one-dimensional direction along sugar/phosphate backbone.

4. Conclusions

The resonant excitations from P 1s to valence unoccupied orbitals in DNA are followed by spectator-type Auger decays where the excited electrons remains in valence orbitals during the core-hole decays. It was also found that the energy of the P $KL_{2,3}L_{2,3}$ spectator Auger peak shifts linearly with the photon energy. The energy difference between spectator and normal Auger peaks goes up to 6.5 eV. These tendencies are quite different from the Auger decay processes in metallic and semi-conducting materials. We conclude that the DNA are wide band-gap insulator in one-dimensional direction along sugar/phosphate backbone.

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