

Localization of electrons in the sugar/phosphate backbone in DNA investigated via resonant Auger decay spectra

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In order to elucidate the localized nature of electrons in sugar/phosphate backbone in DNA molecules, resonant Auger decay spectra excited by soft x-rays around the inner-shell ionization thresholds have been measured for single-strand DNA. The systems investigated are thin films of DNA as well as related phosphorus compounds such as nucleotide (adenosine triphosphate, ATP), sodium phosphate, and indium phosphide. For ATP and DNA, it was observed that the resonant excitations from P 1s to valence unoccupied π^* orbitals are followed by spectator-type Auger decays where the excited electrons remain in valence orbitals during the core-hole decays. It was also found that the energy of the P $KL_{2,3}L_{2,3}$ ($2p^{-1} \cdot \pi^*$) spectator Auger peak shifts linearly with the photon energy due to the resonant Auger Raman scattering. Most of the decay channel at the core-to-valence resonant excitation is spectator-type Auger decay in DNA, which is quite different from the Auger decay processes in metallic and semiconducting materials. We conclude that the excited electrons in valence unoccupied states around the phosphates in DNA molecules are strongly localized, resulting in the insulating properties in a one-dimensional direction along sugar/phosphate backbone.

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I. 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 electric property of DNA thin films deposited on solid surfaces. For the past few years, there have been many experimental and theoretical works concerning the electronic conductivity and electron transport in DNA films.¹ However the reported results are diverse in a wide range: insulating,^{2,3} semiconducting,⁴⁻⁷ metallic,⁸⁻¹¹ and even superconducting.¹² In addition, there are many factors that influence DNA conductivity such as length of molecule, surrounding water molecules, and microstructure.¹ The average conductivity in a DNA film can be measured by general four-probe methods. However, 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. Microspectroscopic methods are effective in elucidating electric conductivity because they provide information about band gaps without directly contacting electrodes. However, the spatial resolution has not come up to a molecular level.

Resonant photoemission spectroscopy as well as resonant Auger electron spectroscopy is one of the suitable methods for the characterization of electric properties as well as electronic structures in solid surfaces. Especially, resonant Auger decay spectra following the photoexcitation around the core-level ionization threshold provide valuable information about the electric properties at a localized atomic site in solids. Up to now, resonant Auger decay spectra following core-level photoexcitation around the inner-shell ionization thresholds have been measured for various condensed systems such as

insulators,¹³⁻¹⁷ semiconductors,¹⁸⁻²⁰ metals,^{21,22} and adsorbed molecules.^{23,24} These works have revealed that the resonant Auger decay spectra exhibit quite different behavior depending on the electric properties of the solid. For metallic and semiconducting solids, the resonant Auger peak turns into normal Auger peak when we increase the excitation photon energy over the inner-shell ionization threshold. For insulating solid, on the other hand, the kinetic energy of the resonant Auger peak is different from that of the normal Auger peak. It was also reported that the energy widths over which the dispersions in resonant Auger peaks are observed are a measure of the localized nature of electrons in empty states.²⁵

Recently, Kato *et al.* have reported the resonant photoemission spectra for DNA at the nitrogen *K*-edge photoexcitation and concluded that the charge-hopping model is pertinent for the electric conduction in a DNA duplex.²⁶ Their work has shown the electric conduction along the base pair stack. Since the nitrogen atoms are included only in the bases, not in molecular backbones, it is also important to elucidate the charge transport mechanism along the molecular skeleton. Compared with the electric conduction along nonperiodic base pair stacks, a sugar/phosphate backbone is another way to carry electrons because it is pure periodic one-dimensional chain with low electron scattering. Actually, it has been pointed out that the low-activation energy of charge transport cannot be interpreted by the electron hopping along the π stack.¹ Endres *et al.* have proposed a possibility that the electric conduction is associated with the sugar/phosphate backbone.¹

In the present paper, we first report on the x-ray absorption spectra and x-ray photoemission (XP) spectra for thin films of DNA and related phosphorus-containing molecules using synchrotron soft x-rays. On the basis of the x-ray absorption spectra, the resonant Auger decay spectra following the phosphorus *K*-edge photoexcitation are presented in or-

der to elucidate the nature of the charge localization around the phosphate. These spectra show the nature of the localized unoccupied states along one-dimensional chain in sugar/phosphate backbone in DNA molecules.

II. EXPERIMENTAL

The experiments were performed at the BL-27A station of the Photon Factory in the High Energy Accelerator Research Organization (KEK-PF) employing double-crystals of InSb(111) plane as a monochromator. The energy resolution of the monochromator was 0.9 eV at 2.1 keV (phosphorus *K* edge). The photon energy was calibrated using the Au 4 $f_{7/2}$ peak in the XP spectra.

High-purity powders of ATP (Wako Pure Chemical Industries Ltd.) and calf thymus single-strand DNA (Merck Ltd.) were used without further purification. The sample was embedded on a surface of an indium plate in order to reduce the charging effect. The samples were introduced into the ultra-high vacuum chamber (base pressure 1×10^{-8} Pa). For comparison, sodium phosphate (insulator) and InP(100) (semiconductor) were also measured as references.

The analysis chamber consisted of a manipulator, hemispherical electron energy analyzer (VSW. CLASS-100), and a low-energy electron flood gun. For the measurements on the Auger decay spectra, the analyzer was operated under the fixed analyzer transmission (FAT) mode. The photon beam was irradiated at 55° from the surface normal, and the electron takeoff direction was surface normal. The x-ray absorption spectra were measured by plotting a sample current as a function of photon energy. The sample current was normalized by the photon intensity measured by the drain current of aluminum foil located in front of the sample.

III. RESULTS AND DISCUSSION

First we show the x-ray photoemission spectra for DNA thin films in order to confirm the chemical states and its stability against x-ray irradiation. Figure 1 shows the wide scan and narrow scans of x-ray photoemission spectra for DNA films. All spectra were shifted by a few eV to lower kinetic energy due to the positive charge at the surface. But this energy shift was constant during the measurements, so the spectra were aligned using the reported binding energy of organic compounds.²⁷ Although carbon and nitrogen atoms in DNA have variety of chemical states, carbon atoms are located in aromatic ring of bases and in aliphatic pentagon of sugar, and nitrogen atoms are located in pyrimidine rings. The C 1s and N 1s binding energies are in agreement with those of the related organic compounds within the experimental errors.²⁷ No contaminations such as carbonates and NO_x are observed. Oxygen atoms in a DNA molecule are located in phosphate, sugar, and bases (thymine, guanine and cytosine). The O 1s binding energies of phosphate²⁸ and bases²⁹ are located around 530 eV, which are in good agreement with our data. Although the O 1s binding energies for sugar or ribose have not been reported to the best of our knowledge, the O 1s binding energies for similar compounds such as hydroxyquinoline are located at 530.9 eV,³⁰ which is

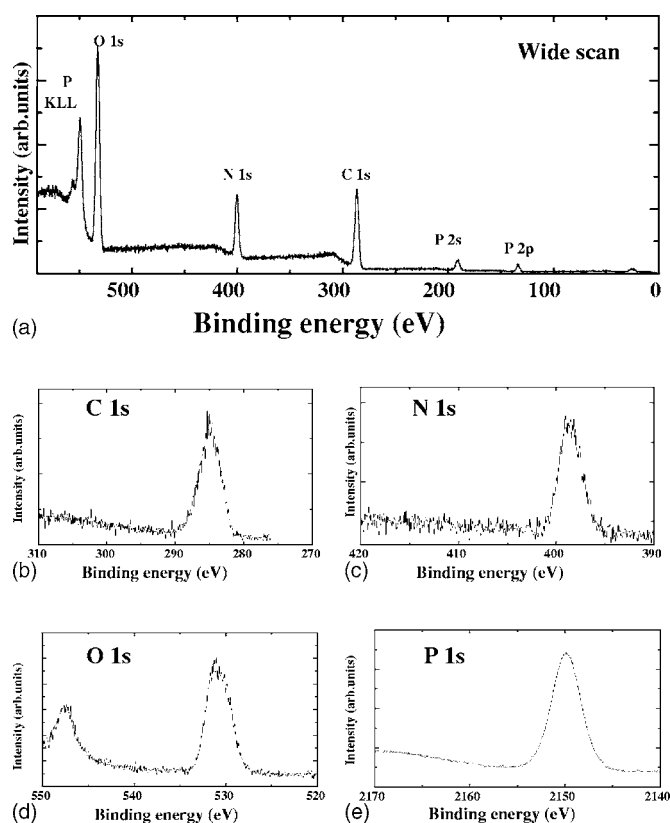


FIG. 1. X-ray photoemission spectra excited by 2400 eV photons for DNA molecule: (a) wide scan, (b) carbon 1s, (c) nitrogen 1s, (d) oxygen 1s, and (e) phosphorus 1s regions.

also close to our data. The O 1s spectrum shows that there is no contamination of water. So the electron spectroscopic data shown hereafter are those for water-free, dry DNA molecules. The similar photoemission results have been obtained for ATP molecules.

It is known that the organic and biological molecules are sensitive to the radiation, and they would sometimes easily decompose when exposed to intense x-ray beam. In order to check the stability of ATP and DNA molecules, the molecules were exposed to 3 keV x-rays for one day (up to 10^{15} photons/cm²). As a result, any changes in the spectral patterns were not observed. The results suggest that ATP and DNA molecules are stable against x-ray irradiation at least in the present photon flux.

Figure 2 shows phosphorus *K*-edge x-ray absorption spectra for ATP and DNA together with those for the phosphorus-containing reference compounds sodium phosphate and indium phosphide. Phosphorus atom in sodium phosphate has a chemical environment that is similar to those of ATP and DNA. Indium phosphide was chosen as a typical semiconductor material containing phosphorus atom. 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. In phosphate, the phosphorus atom in PO₄³⁻ anion is coordinated to four oxygen atoms approximately with *T_d* symmetry. This is the same situation as P₄O₁₀ and PO(C₆H₅O)₃, whose P *K*-edge x-ray absorption spectra have been reported and interpreted by MS (multiple scatter-

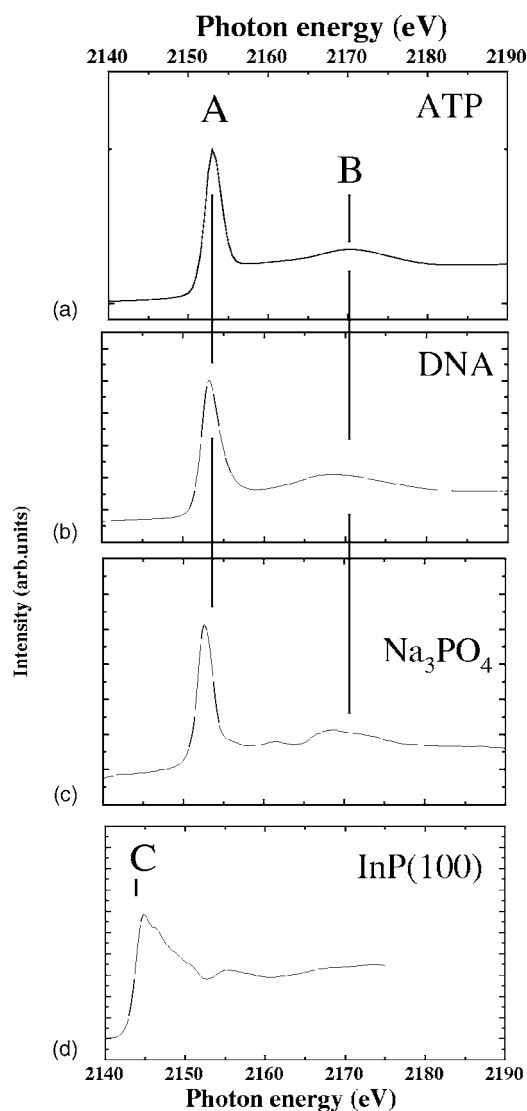


FIG. 2. X-ray absorption spectra for (a) ATP, (b) DNA, (c) sodium phosphate, and (d) InP(100). The spectra were measured by total electron yield.

ing) x-alpha calculations.³¹ Considering the dipole selection rule, peak A is due to the excitation from P 1s into P 3p-derived orbitals (t_2^*) and the higher-energy peak B is originating from shape resonance into the orbitals with d character.³²

The x-ray absorption spectrum for InP(100) is the same as the reported one.³³ The spectrum was interpreted by full multiple scattering calculations.³³ The energy of the first resonance peak (marked C) is lower by 7.0 eV than those for phosphate. The higher resonance energy in DNA spectrum may be related to the insulating properties of DNA molecules, because conduction bands above the Fermi level in insulator are located at higher energy than those in semiconductors and metals. However the resonance energy in x-ray absorption spectrum depends not only on the energy level of the conduction band but also on the other parameters such as initial core-level energy and screening effect. Thus, it is needed to measure resonance Auger electron spectra in order to clarify the electric property in localized regions.

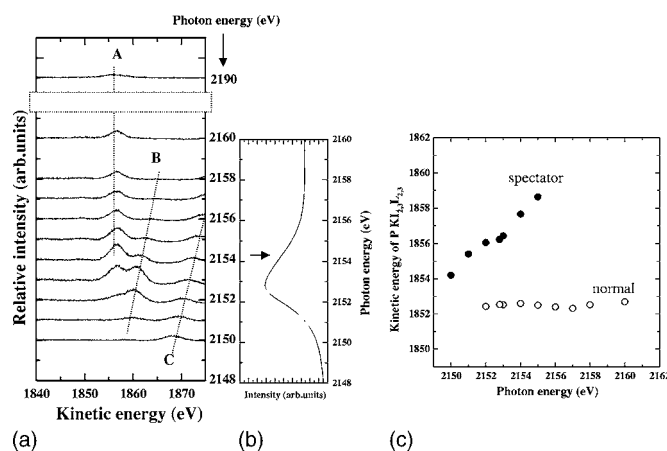


FIG. 3. (a) Phosphorus $KL_{2,3}L_{2,3}$ resonant Auger decay spectra for DNA molecule. Peak A with constant kinetic energy is due to normal Auger decay, whose initial state is $2p^{-2}$. Peak B is originating from spectator Auger decay of which initial state is $2p^{-1} \cdot \pi^*$. Peak C is due to 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.

Since similar results were observed for DNA and ATP, we will hereafter concentrate on the Auger decay spectra for DNA molecules. Phosphorus $KL_{2,3}L_{2,3}$ resonant Auger decay spectra for DNA following phosphorus K-edge excitation are displayed in Fig. 3(a) together with the x-ray absorption spectrum [Fig. 3(b)]. The ionization threshold is shown as arrow in the x-ray absorption spectrum. 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, whose initial states are $2p^{-2}$. 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 ($hn=2153$ eV). The intensity of the component B is nearly proportional to the x-ray absorption intensity. In our previous paper, we have observed similar Auger peaks for insulating solids, and elucidated that these peaks are originating from spectator-type Auger decay.¹⁶ The initial state of spectator-type Auger decay is $2p^{-1} \cdot \pi^*$. For $KL_{2,3}L_{2,3}$ ($2p^{-1} \cdot \pi^*$) spectator Auger decay in third-row elements, a core electron in the 1s orbital is resonantly excited into the valence unoccupied orbitals, and an electron from the 2p orbitals decays into the core hole, and then another electron in the 2p orbital is emitted as Auger electron.

The process in spectator Auger decays has been well investigated for solids with various electric properties from insulators¹³⁻¹⁷ to metals.^{21,22} It has been elucidated that the Auger peaks for insulator are split into two components, spectator and normal Auger peaks, and the most of the decay channels around the core-to-valence resonance excitation is spectator-type Auger decay. For semiconductors, the relative intensity of spectator-type Auger decay is small,¹⁹ and for metals only a single Auger peak is observed.²² In the case of

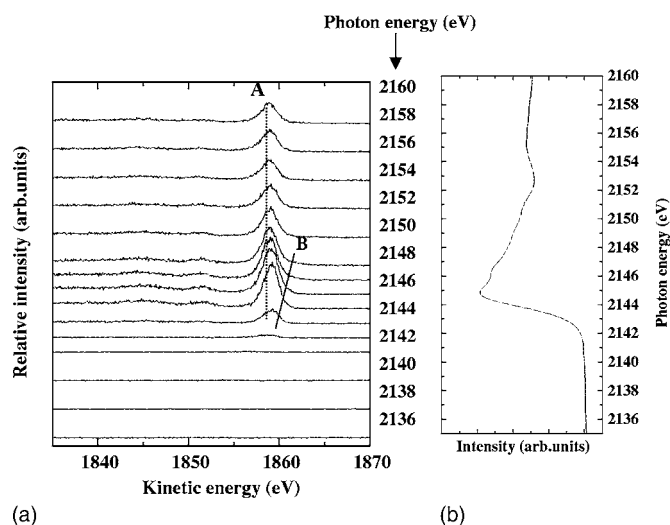


FIG. 4. (a) Phosphorus $KL_{2,3}L_{2,3}$ resonant Auger decay spectra for InP(100). (b) X-ray absorption spectra around the phosphorus K edge for InP(100).

metals and semiconductors, the time scale of the delocalization of the excited electrons is fast in comparison with the Auger electron emission due to the screening effect of the conduction electrons in the Fermi level. We confirmed this property for semiconducting InP(100), which is shown in Fig. 4. A small spectator peak is seen as shoulders (marked *B*), but the relative intensity of this peak is negligibly small compared with that in DNA. The energy splitting of the resonant Auger peak is due to the localization of excited electrons in valence unoccupied orbitals during the Auger decay. Clear peak splitting in Fig. 3 suggests that the DNA molecules have insulating properties around the phosphate backbones.

Another outstanding phenomenon seen in Fig. 3 is the energy shift of spectator Auger peaks. In Fig. 3(c), the kinetic energy of the Auger peaks is plotted as a function of the incident photon energy. In contrast to the normal Auger peaks with constant kinetic energy, the energy of 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.¹⁵ 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 a wide energy range in insulating solid compared with semiconductor or metal if the excited electrons are localized in unoccupied orbitals. Actually, it was also reported that the energy

widths over which the dispersions occur in resonant Auger peaks are a measure of the localized nature of electrons in empty states.²⁵ 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. Although the present results do not present information about the electron migration mechanism along the base pair stack, our data reveal that the excited electrons in valence unoccupied states around the phosphates in DNA molecules are strongly localized in the time scale of the Auger decay. Such localization of electrons in valence unoccupied states results in the insulating properties of DNA in one-dimensional direction along the sugar/phosphate backbone.

It should be noted that the electric properties of thin films deposited on a substrate may change depending on the interaction with the substrate due to the charge screening by the substrate. So the measurements on the resonant Auger decay spectra for ultrathin films at molecular scale on substrates are important in order to elucidate the electric properties of biofilms, which is now in progress. Also the measurements on water-adsorbed DNA molecules are needed to simulate the nature of electron localization in live biological systems.

IV. CONCLUSION

We have measured the resonant Auger decay spectra excited by soft x-rays around the phosphorus K edge for single-strand DNA molecules as well as some of the reference compounds in order to elucidate the localized nature of electrons in one-dimensional sugar/phosphate backbone of DNA molecules. For ATP and DNA, it was observed that the resonant excitations from $P 1s$ to valence unoccupied π^* orbitals are followed by spectator-type Auger decays where the excited electrons remain in valence orbitals during the core-hole decays. It was also found that the energy of the $P KL_{2,3}L_{2,3}$ ($2p^{-1} \cdot \pi^*$) spectator Auger peak shifts linearly with the photon energy due to the resonant Auger Raman scattering. Most of the decay channel at the core-to-valence resonant excitation is spectator-type Auger decay in DNA, which is quite different from the Auger decay processes in semiconducting indium phosphide. We conclude that the excited electrons in valence unoccupied states around the phosphates in DNA molecules are strongly localized, resulting in the insulating properties in one-dimensional direction along the sugar/phosphate backbone.

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