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Observation of Photopyroelectric Signal in X-Ray Region

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Photopyroelectric (PPE) signal induced by X-ray absorption in a copper foil could be observed by using a thin ferroelectric polyvinylidene difluoride film with aluminium electrodes. An EXAFS was found in each PPE signal intensity and phase spectrum.

PPE spectroscopy is based on detection of a change in temperature resulting from optical absorption in condensed phases.[1-2] It has been shown that PPE detection using thin ferroelectric polyvinylidene difluoride (PVDF) films had a response time of less than 100 ns and spectroscopic detectability equivalent to one monolayer of Nd_2O_3.[1)] On the other hand, heat generation in solids on X-ray absorption was detected by a microphonic photoacoustic method[3)] and photoacoustic EXAFS have been observed.[4,5)] For further examination of the heat generation on X-ray absorption, alternatives different from the microphonic method have been desired. In this work, the PPE detection is tested in the X-ray region.

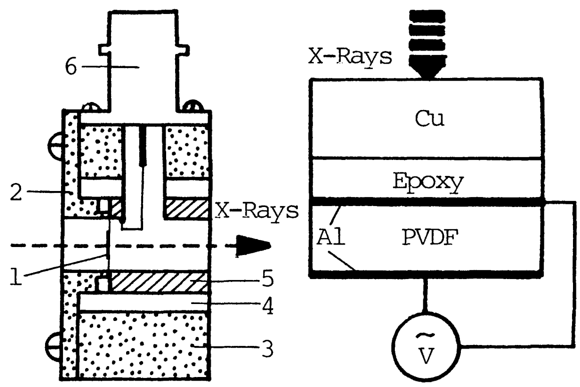

Fig. 1. Cross sectional view of PPE cell and schematic illustration of sample 1, Cu foil attached onto PVDF film; 2, brass holder being in contact with a positively polarized side of PVDF film; 3, brass cell body; 4, Teflon insulator; 5, brass holder being in contact with a negatively polarized side; 6, connector.

The experimental arrangement for the proposed PPE detection was quite similar to that for the X-ray photoacoustic detection using a microphone.[3] The experiments were performed with the use of X-rays from the electron storage ring at Photon Factory (Beam Line BL 4A) in the National Laboratory for High Energy Physics. A sample of a 10-μm-thick Cu foil (Nilaco, CU-113173) was carefully attached onto a positively polarized side of the 9-μm-thick PVDF film (Kureha Industry Co., Ltd., KF piezofilm) with epoxy cement (GRACE JAPAN K.K, STYCAST 1266) so that the epoxy cement formed a ca. 5-μm-thick uniform layer. The Cu foil attached onto the PVDF film was held between two metal holders separated electrically each other by a Teflon cylinder, as shown in Fig. 1. Two ion chambers were placed before and behind the Cu foil in order to obtain absorption and PPE spectra simultaneously. The monochromatic X-rays from the storage ring were chopped by a rotating lead plate at 30 Hz. The intermittent X-rays passing through the first ion chamber entered into the Cu foil, the epoxy cement layer, and the PVDF film in this sequence and reached the other ion chamber. A fraction of X-ray energy absorbed in the Cu foil is converted into heat, which is carried into the PVDF film by thermal diffusion. The periodic change in temperature resulting from the intermittent irradiation induces the corresponding change in polarization of the PVDF film and finally leads to a voltage signal. The voltage signal was amplified by a preamplifier (PAR, 113) and a lock-in amplifier (NF, 5610). A wave form of the signal from the preamplifier was directly monitored with a digital storage oscilloscope (Tektronix, 2440).

Figure 2 shows wave forms of PPE signals observed at 9011 eV (a)

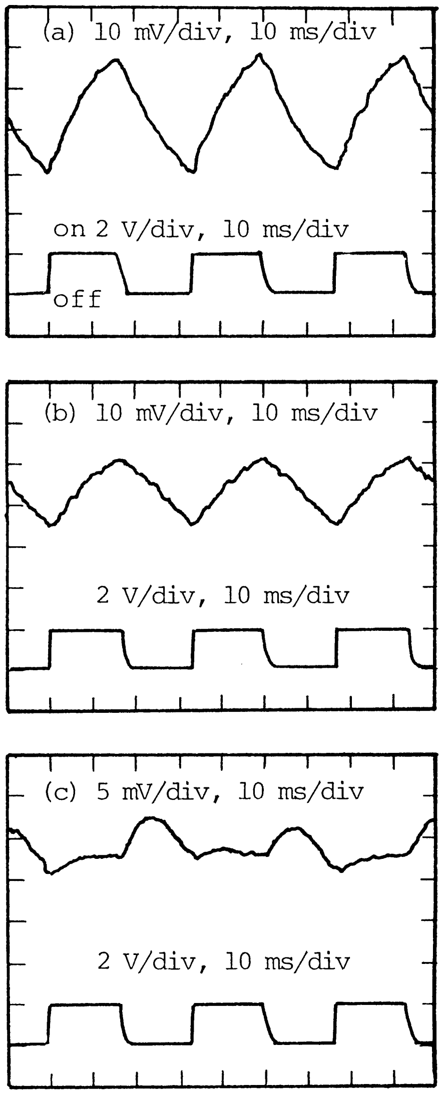

Fig. 2. X-Ray PPE signals (a) at 9011 eV for the 10-μm-thick Cu foil attached onto the PVDF film, (b) at 8955 eV for the same sample as (a), (c) at 8796 eV for the PVDF film with the ca. 5-μm-thick epoxy cement layer. The upper and the lower wave forms show the PPE signal and the chopping signal, respectively. On and off mean irradiation and interruption of X-rays.

and 8955 eV (b), which are energies above and below the K-edge of Cu, for the 10-μm-thick Cu foil attached onto the PVDF film and at 8796 eV for the PVDF film with the epoxy cement layer (c). The saw wave forms similar to those for the photoacoustic detection using a microphone were observed for the Cu foil, (a) and (b).[3] The magnitude at 9011 eV is larger than that at 8955 eV, as can be seen in Fig. 2, indicating that the magnitude increases with the increasing absorption coefficient. While the signal for the PVDF film (c) showed an unusual form having a small rising on irradiation and a sudden hump on non-irradiation. It was suggested from comparison of wave forms for the PVDF films with and without the epoxy cement layer that the hump on non-irradiation was due to existence of the epoxy cement layer but its detail was unclear. The signal from the epoxy cement layer has a possibility to deform the PPE signal for the Cu foil attached onto the PVDF film as well. Since the epoxy cement layer was practically covered with the Cu foil, the signal might be deformed depending on the absorption coefficient, that is, the X-ray energy. In fact the wave form at 8955 eV (b) shows a slight deformation (hump) on non-irradiation compared with that at 9011 eV. In spite of the fact that the signal from the epoxy cement layer hinders exact PPE observation of the sample, this signal implies that the proposed PPE detection may give a method by which some photo-induced phenomena other than the photothermal effect can be examined in the X-ray region.

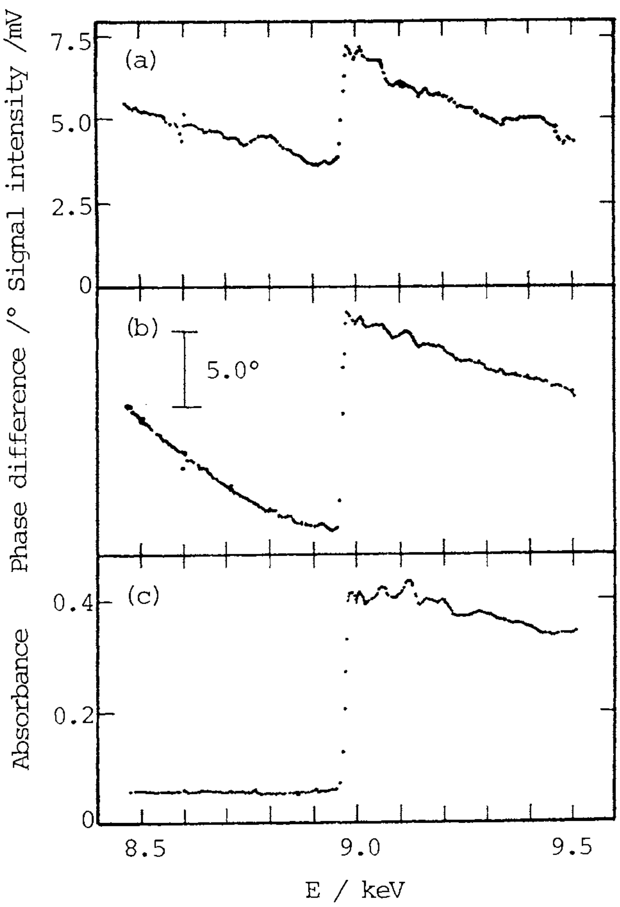

Fig. 3. X-Ray PPE spectra and absorption spectrum
(a) signal intensity spectrum, (b) phase spectrum, (c) absorption spectrum; sample, 10-μm-thick Cu foil; gain of preamplifier, 100; chopping frequency, 30 Hz.

Figure 3 shows the PPE signal intensity (a) and the PPE phase (b), and the absorption (c) spectrum for the 10-μm-thick Cu foil. (The slow variations in the signal intensity spectrum are essentially due to variation of the incident X-ray intensity.) In the similar manner to the absorption spectrum, each PPE spectrum showed the EXAFS of Cu following the sharp rising at the K-edge. However the spectra were significantly different in shape from one another. Although these findings suggest that the PPE signal is closely related with the absorption coefficient, it seems to be difficult to explain the PPE spectra straightforwardly. PPE spectroscopy has been theoretically explained in the ultraviolet and visible region in terms of diffusion of heat generated by an optical absorption.[6] On the other hand, a microscopic theory has been proposed in X-ray photoacoustic spectroscopy, taking into account complex electronic thermalization processes involved in heat generation.[7] A theoretical study of these PPE spectra is now in progress.

In conclusion, the PPE detection using a thin PVDF film has proved applicable to the detection of heat generated by the X-ray absorption. Because of transparency of the film to the X-rays, the PPE spectrum could be readily obtained for a sample attached onto the film. As it is expected that the PVDF film detector has a fast response time and high sensitivity[1] and can be used in vacuum, the proposed PPE detection will be a useful alternative for the examination of photothermal processes following the X-ray absorption in materials.

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