Observation of chemical shifts of Si 2p level by an x-ray photoelectron spectroscopy system with a laser-plasma x-ray source

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An x-ray photoelectron spectroscopy system with a laser-plasma x-ray source is shown to have energy resolution high enough to observe chemical shifts of Si 2p electrons in SiO$_2$, Si$_3$N$_4$, and pure Si. A boron nitride (BN) plasma x-ray source is produced by irradiation of 100 mJ Q-switched YAG laser pulses. A single line emission at 4.86 nm is selected from the BN plasma by means of carbon foils. Fine spectra are acquired with only 96 laser shots. The results obtained confirm that a laboratory-sized x-ray photoelectron spectroscopy system with submicron spatial resolution and high spectral acquisition speed can be realized. © 1998 American Institute of Physics.

X-ray photoelectron spectroscopy (XPS) is presently the most valuable analytical method to provide information on the chemical states of materials while minimizing sample damage. However, a conventional XPS system is disadvantageous in that spatial resolution is limited to around 10 μm. With the ongoing progress of semiconductor devices and new material technologies, the demand for microanalysis with spatial resolution better than 1 μm is increasing. It is vital to develop a μ-XPS system with submicron resolution. Although many studies have been performed at large synchrotron facilities over the world, a compact system is required to allow in situ observation, which is critical in studies of devices and materials.

The idea of an in-house μ-XPS system employing a laser-plasma x-ray source (LPX) was first proposed by Tomie. Previously, LPX’s pulsing nature, which leads to an emission duty factor as low as 10$^{-6}$ even at 1 kHz operation, was considered to be a serious disadvantage in its application to XPS where high average power is necessary. In Tomie’s patent, however, the pulsing nature of the LPX source is changed to an advantage by adopting the time-of-flight (TOF) method for energy analysis of photoelectrons. The high detection efficiency of the TOF method can compensate for the extremely low duty factor of the LPX source. Moreover, as discussed in detail in Ref. 4, the high reliability of the spectral profiles obtained by employing the TOF method is beneficial in observing impurities and defects of quite low concentration, while the system’s high detection efficiency makes it possible to realize spatial resolution down to the tens of nm region, where resolution is limited by x-ray radiation damage. Another idea to the patent is the monochromatization of the x-ray source without the use of a grating, which would reduce the x-ray intensity on the sample by several orders. We believe that by adopting the TOF method together with the monochromatization with a filter it is possible to realize an in-house μ-XPS system with high acquisition speed comparable to that of a system with an undulator source. We have been performing ongoing research to develop a μ-XPS with a LPX source for practical applications.

In a previous paper, we reported that a LPX-XPS system employing TOF energy analysis can acquire a photoelectron spectrum with a low number of laser shots and that the number of photoelectrons detected was in fairly good agreement with that which would be theoretically expected. In this experiment, the plasma produced on a tantalum target generated a near-continuum spectrum. It’s spectral width was narrowed to 6 eV by means of a multilayer mirror.

In order to obtain detailed information on the chemical states of materials, the energy resolution of an XPS system must be better than 1 eV. Such a high resolution can be realized in a LPX-XPS system. As stated in Tomie’s patent, by means of a simple filter, a single line emission for high-resolution XPS can be selected from a LPX source if the laser irradiation condition is optimized such that several lines, well separated in wavelength, are generated. In this letter, we report an experiment where a high-energy resolution in LPX-XPS system was realized by the monochromatization of x rays with a filter. With this high-resolution system we were able to observe the chemical shifts of Si 2p photoelectrons.

Figure 1 shows our experimental setup. Details are described in Ref. 2. A laser-plasma x-ray source was produced by irradiation of a BN target at a laser energy of 100 mJ and a pulse repetition rate of 1 kHz. By means of carbon foils, a single line emission at 4.86 nm was selected from the plasma and was monochromatized with a simple filter. A single line emission for high-resolution XPS can be selected from a LPX source if the laser irradiation condition is optimized such that several lines, well separated in wavelength, are generated.

FIG. 1. The experimental setup. X rays emitted from a BN plasma were filtered by two Mylar foils and a carbon foil. Photoelectrons emitted from the x-ray-irradiated sample were detected with a MCP after traveling 50 cm through a flight tube. A retarding potential is applied to electrodes to improve the energy resolution of the photoelectron spectrum.

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scribed in Ref. 5. To select a single line with a filter, the x-ray spectrum must match the transmission spectral window of that filter. Since, in our experiment, carbon was used as a filter, the best x-ray spectrum for single line selection is that of boron. We therefore employed a BN sheet for our target.

Figure 2(a) shows the x-ray spectrum from the BN target when the second harmonics of a Q-switched YAG laser of around 100 mJ pulse energy with a 2.5 ns duration irradiated the target at 10¹² W/cm². The spectrum was acquired using a flat-field grating⁶ of 1200 lines/mm and recorded on Kodak 101-01 film. Between 2.5 and 6 nm, there are several strong lines emitted from hydrogen-like and helium-like nitrogen and boron ions.

Lines of shorter wavelength than the carbon K edge at 4.4 nm are eliminated by the use of a carbon filter. A thick carbon filter also reduces the intensity of lines on the long wavelength side far from the carbon K edge. Thus, filtering of the spectrum in Fig. 2(a) by a piece of 2.4-µm-thick Mylar foil results in a single line at 4.86 nm of 255 eV photon energy, as shown in Fig. 2(b). The effect of the weak line remaining at 6.03 nm was negligible in the observed photoelectron spectra, as seen below.

Thus, a single line can be obtained from a LPX source with the use of a filter. The linewidths in Fig. 2 were limited by the resolution of the grating. We believe that the actual spectral linewidth was around 1/1000 of the wavelength observed. With a conventional spectrometer, however, such a narrow linewidth is very difficult to observe.

With the single line emission thus obtained, we should be able to observe chemical shifts. A silicon wafer with patterned lines of silicon dioxide (SiO₂) and a silicon wafer with patterned lines of silicon nitride (Si₃N₄) were used as test samples. The patterned lines were about 1 mm wide and 100 nm thick. The distance from the LPX source to the sample was 50 mm. The irradiated area on each sample was about 5 mm in diameter. Both the patterned lines and the exposed Si substrate were irradiated. After traveling 50 cm through the flight tube, photoelectrons emitted from the sample were detected by a microchannel plate (MCP). The pressure in the target chamber was about 10⁻⁵ Torr and that in the flight tube was about 3 × 10⁻⁶ Torr. The filter foils used to select the single line emission also served to vacuum isolate the flight tube from the x-ray generation target chamber.

Figure 3 shows overlaid photoelectron spectra from two test samples. As reported in Ref. 5, photoelectron energy resolution in TOF can be improved by applying a retarding field. The spectra illustrated in Fig. 3 were obtained with the retarding voltage of 135 V. Each spectrum was acquired by averaging the data of 96 laser shots. The three peaks in Fig. 3 correspond to photoelectrons emitted from the 2p state of silicon in SiO₂, Si₃N₄, and pure Si. The observed chemical shift of the Si 2p in the SiO₂ from the pure Si was about 4.5 eV and that in the Si₃N₄ was about 2.5 eV. These chemical shifts are the same as reported using a conventional XPS system.⁸ Thus, we have demonstrated that a LPX-XPS system can have an energy resolution high enough to observe chemical shifts.

As stated above, the spectra shown in Fig. 3 were obtained by averaging data from 96 laser shots. At present, our system is not designed to operate at a high repetition rate. However, we do not foresee any serious problems in operating the laser at 100 Hz repetition in a future system. At such a repetition rate, the spectra in Fig. 3 could be acquired in only 1 s.

Now, we discuss the photon flux on the sample. From the x-ray spectrum in Fig. 2(b), we know the x-ray intensity, and we can estimate that the number of photons in the 5 mm diameter irradiation area on the sample was 7 × 10⁹ photons/pulse. If the LPX is operated at 100 Hz, we will attain 7 × 10¹⁰ photons/s on the sample. Such a photon

FIG. 2. (a) Spectrum of x rays emitted from a BN plasma and (b) that of x rays transmitted through a 2.4-µm-thick Mylar foil. The single Lyman α line of boron ions at 4.86 nm of 255 eV photon energy was selected by means of a single Mylar foil.

FIG. 3. Photoelectron spectrum from a silicon wafer with patterned lines of SiO₂ overlaid with that from a silicon wafer with patterned lines of Si₃N₄. Each spectrum was obtained by averaging the data from 96 laser shots. The retarding voltage was 135 V. The three peaks correspond to photoelectrons emitted from the 2p state of silicon in SiO₂, Si₃N₄, and pure Si, respectively.
flux is comparable to that achieved using a synchrotron source.\(^8\)

Our estimation of the photon flux on the sample for our LPX source can be confirmed by the photoelectron signal detected. From the above estimation, about 600 electrons/pulse are calculated to reach the MCP by the procedure described in Ref. 5. This number is when no retarding field is applied. When a retarding field is applied to improve energy resolution, the effective solid angle for the detection of photoelectrons decreases, since only the axial velocity is reduced by the retarding field and velocity components perpendicular to the axis of the flight tube are not affected. When the retarding field is 135 V, the effective solid angle will be reduced to about one seventh. Therefore, under the experimental conditions for the results shown in Fig. 3, we calculate that about 86 electrons/pulse should reach the MCP. The current signal of the MCP detector can be converted to the number of detected electrons per 1 eV bandwidth. In the case of both the SiO\(_2\)/Si and the Si\(_3\)N\(_4\)/Si samples, the total number of Si 2\(p\) photoelectrons for each spectrum is about 80 electrons/pulse. Thus, we confirm that the observed number of photoelectrons shown in Fig. 3 agrees well with that expected from the irradiation intensity of the x rays with the spectrum shown in Fig. 2(b).

In summary, we have demonstrated that a single line emission can be obtained from a LPX source by the use of a simple filter with a well-matched x-ray spectrum. Successful observation of chemical shifts of Si 2\(p\) electrons in SiO\(_2\), Si\(_3\)N\(_4\), and pure Si showed that the selected single line at 4.86 nm of 255 eV photon energy had a spectral width better than 1 eV. X-ray intensity and photoelectron signals showed that an x-ray flux as high as \(7 \times 10^8\) photons/shot irradiated the 5 mm diameter area on the sample. By experimentally observing that fine photoelectron spectra were obtained with only 96 laser shots, we confirmed our claim that our LPX-XPS system can achieve a high data acquisition speed comparable to that with a synchrotron source.