CHEMICAL STRUCTURE AND SURFACE POTENTIAL OF NICKEL AND NICKEL-OXIDE THIN-FILM SURFACES STUDIED BY HIGH-RESOLUTION MONOCHROMATED X-RAY PHOTOELECTRON SPECTROSCOPY AND SCANNING KELVIN FORCE MICROSCOPY

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Nickel and its oxide states are of both technological and scientific importance, and have seen wide use as catalysts for the formation of synthesis gas from methane.1)-3) They have also been received attention due to their catalytic ability to produce a wide variety of carbon-related nanomaterials, such as carbon vermicules that show a bifilamentary or tubular structure of carbon deposits,4),5) graphite whiskers that are cylindrical, hollow, and tube-like,6) and so-called “carbon tubes” with nanometer-size diameters.7),8) We have been interested in the unique reactivity of nickel to carbon as a key factor for ‘hexagonal’ diamond synthesis.9) The physico-chemical properties of nickel and its oxide surfaces play essential roles in yielding the reactivity for useful carbon-related material synthesis in these systems. We investigated the relation between the chemical structures of nickel-oxide (NiOx) thin-film surfaces and their surface potentials by high-resolution monochromated X-ray photoelectron spectroscopy (HRXPS) and scanning Kelvin force microscopy (KFM). Our motivation for studying the surfaces of nickel and oxide surfaces stems from their unique reactivities, which are effective for a variety of carbon-related material syntheses.

The NiOx thin-films were deposited by a magnetron sputtering method using a Ni metal target with a mixture of Ar and oxygen as the sputtering gas. The flow ratio of oxygen to the mixture sputtering gas was varied from 0 to 50% to control the composition of nickel and oxygen in the sputtered films. The total flow rate of the gas mixture was 40 sccm and the sputtering pressure was 0.5 Pa. The input DC sputtering power was 1.0 kW.

The surface chemical structure of the sputtered thin-films were measured by high-resolution monochromated X-ray photoelectron spectroscopy (HRXPS; VG Scientific, UK). The XPS spectra were excited by Al $K\alpha$ radiation with an instrumental resolution of 0.5 eV. The X-ray beam was focused at a 500 µm-diameter point on the surface to be measured. A high-purity (5N) nickel polycrystalline sheet was also measured to obtain the standard spectrum of a nickel metal.

The surface potentials of the nickel and nickel-oxide surfaces were measured by scanning Kelvin force microscopy (KFM; SPI-3700, Seiko Instruments, Japan.) in air. The surface potential of NiOx corresponds to the surface electronic states, in other words, it indicates the surface reactivity. A micro-cantilever was used as the Kelvin probe for these measurements. The cantilever was made from single-crystal silicon coated with gold film for electrical conduction and chemical inertness. The spring constant and the resonant frequency of the cantilever were 1.6 N/m and 20 kHz. The scanned area was 10 µm square and the distribution of the surface potential value was obtained using a grid of 256 x 256 data points. The histogram of the data points showed one peak and was symmetrical in shape because the measured areas were almost uniform. The peak value of the histogram was determined as the surface potential of the scanned area. Five different areas were measured on each of the surfaces to confirm the generalizability of the measured values.

As shown in Fig. 1, the XPS spectra revealed the coexistence of a nickel metal state consisting of Ni, NiO, and Ni_2O_3 on the NiOx thin-film surfaces. The surface potential varied with the variation of the NiOx oxidation states; the nickel metal surface showed a much higher surface potential (330.5 mV) compared to the nickel-oxide thin film surface (-8.9 mV). The difference in surface potential due to a charge transfer between nickel and oxygen was equivalent to that in the electronic structure of the surface. The surface potential may be controlled by a modification of the NiOx oxidation states. The surface potential of NiOx uniquely affects the synthesis of carbon-related materials. An understanding of the relation between the chemical structures of NiOx surfaces and the variation in their surface potentials will lead to controlled, desired catalytic reactivities for synthesis gas formation and carbon nanotube growth, and new approaches for diamond growth.

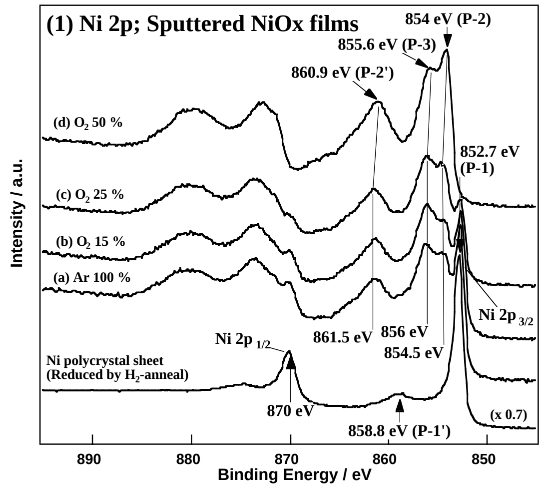

Fig. 1 XPS spectra of the sputtered NiOx surfaces

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