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Short communication

Optimizing coverage of metal oxide nanoparticle prepared by pulsed laser deposition on nonenzymatic glucose detection

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ABSTRACT

Metal oxide nanoparticles prepared by pulsed laser deposition (PLD) were applied to nonenzymatic glucose detection. NiO nanoparticles with size of 3 nm were deposited on glassy carbon (GC) and silicon substrates at room temperature in an oxygen atmosphere. Transmission electron microscope (TEM) image showed nanoparticles with the size of 3 nm uniformly scattered on the Si(0 0 1) substrate. Unlike co-sputtering nanoparticle and carbon simultaneously, the PLD method can easily control the surface coverage of nanoparticles on the surface of substrate by deposition time. Cyclic voltammetry was performed on the samples deposited on the GC substrates for electrochemical detection of glucose. The differences between peak currents with and without glucose was used to optimize the coverage of nanoparticles on carbon electrode. The results indicated that optimal coverage of nanoparticles on carbon electrode.

1. Introduction

Nickel oxide (NiO) has been investigated for its immense potential in a wide range of applications due to its unique magnetic, catalytic and electronic properties. Nanoparticles of NiO have received significant attention; it is known to be super paramagnetic, for example [1]. Nanoparticles have been prepared by a variety of methods such as electrochemical deposition [2–6], sputtering [7–9], and pulsed laser ablation (PLD) [10–12]. Among these methods, the PLD method has the advantage of flexibility of deposition in a wide range of vacuum pressures and especially in control of concentration of nanoparticles.

Transition metals applied to electrochemical detection (ECD) as a working electrode can detect glucose directly without glucose oxidase (nonenzymatic glucose detection). As an application of nanoparticle catalyst, You et al. [7] prepared a working electrode by co-sputtering of Ni and carbon on glassy carbon (GC), and used the electrode for ECD with constant potential amperometric method. Since co-sputtering buries nanoparticles in the carbon film, nanoparticles underneath the top surface did not affect catalytic process in these electrodes. Although nanoparticle on the top surface strongly contributes to catalysis, it is difficult to control the concentration of nanoparticles on top surface by the co-sputtering method.

The PLD method has been used to prepare nanoparticles [11,13], however, it has not been applied to the field of ECD. In this study, nanoparticles were prepared by the PLD method and were used for ECD of glucose as a working electrode. The nanoparticles were prepared on GC and silicon substrates so that the surface coverage of nanoparticles on the top surface of substrate could be easily controlled by the deposition time. Nanoparticles can be deposited on only topmost surface by the PLD method instead of implanting the nanoparticles in films using the co-sputtering method. The PLD method has the advantages of (1) controlling the size of nanoparticle [11,13,14], (2) high efficiency as catalyst due to modification of only the top surface, (3) quite short modification time (less than 1 min) compared to other methods ECD was performed using the electrodes with varying deposition time to detect glucose in alkaline media. To investigate the effect of a catalyst of NiO nanaoparticles, the differences of peak currents were evaluated on with and without glucose in alkaline media.

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Table 1
Summary of laser deposition conditions. Carbon and silicon(0 0 1) substrate were used for glucose detection and TEM observation, respectively.

Target	Carbon substrate Silicon(0 0 1) substrate
Laser	Slower Q-switched YAG[a]
Wavelength	266 nm
Repetition rate	2 Hz
Laser fluence	~2 J/cm^2
Distance to target	30 mm
Gas pressure	10 Pa (oxygen)
Deposition time	2 s to 2 min

[a] See Ref. [15] for details of the slower Q-switched YAG.

2. Experimental

Nanoparticles were prepared on GC and Si substrates at room temperature by using the slower Q-switched Nd-YAG pulsed laser (Spectron Laser System SL803) [15]. The fourth harmonic (266 nm) was used at the repetition rate of 2 Hz with an energy fluence of ~2 J/cm^2. Substrates of both Si(0 0 1) and glassy carbon (GC) were prepared to the size of 10 mm × 10 mm, and were placed with a distance of 30 mm from the target in an oxygen pressure of 10 Pa. The nickel (II) oxide targets with $\phi = 10$ mm and thickness of 5 mm were purchased from Kojundo Kagaku (Saitama, Japan). The target was rotated and swung during ablation and the ablation time varied from a few seconds to 2 min on glassy carbon. Table 1 shows summary of deposition conditions.

After the nanoparticles were prepared on Si(0 0 1) substrates, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were employed to evaluate crystal structure and atomic composition. PANalytical Xpert MRD and ULVAC PHI 5500 were used for XRD and XPS, respectively. Auger electron spectroscopy (AES; ULVAC PHI 670 Auger NanoProbe) was also employed to analyze the surface of samples. Scanning electron microscopy (SEM; FEI SIRION 200) and atomic force microscopy (AFM; SII Probe Station SPI 3800) were used to evaluate surface morphology, and the size of nanoparticle was examined by transmission electron microscope (TEM).

Cyclic voltammetry (CV) measurements were performed with a three-electrode cell consisting of NiO nanoparticles prepared on the GC substrate as the working electrode ($d = 7.4$ mm), an Ag/AgCl reference electrode and a platinum auxiliary electrode. CV measurements were performed in 0.1 M NaOH solution and in the presence of 1 mM glucose with scan rate of 50 mV/s. The water used in this study was purified by Milli-Q (Millipore, Bedford, MA).

3. Results and discussion

Nanoparticles were deposited on Si(1 0 0) substrates in an oxygen pressure of 10 Pa with a deposition time from 5 s to 5 min. The Si peak in the XPS spectra disappeared on the sample with ablation time at more than 3 min. The surface roughness estimated by AFM rapidly improved at deposition time of 3 min. Together these indicated the surface was fully covered as like NiO film deposited on Si substrate. The roughness at 3 min ablation showed $R_a \sim 0.24$ nm, which is coincident with smooth surface of NiO thin film in previous studies [9].

NiO thin films prepared at room temperature show epitaxial growth [10] in certain range of oxygen pressure. The crystallinity is dependent on oxygen pressure during the deposition process, and NiO films epitaxially grow at around 1 Pa of oxygen atmosphere. For CV analysis using NiO thin film as an electrode, amorphous NiO shows higher sensitivity than crystal NiO film [16]. XRD showed amorphous structure on NiO thin film prepared using the PLD method in this study.

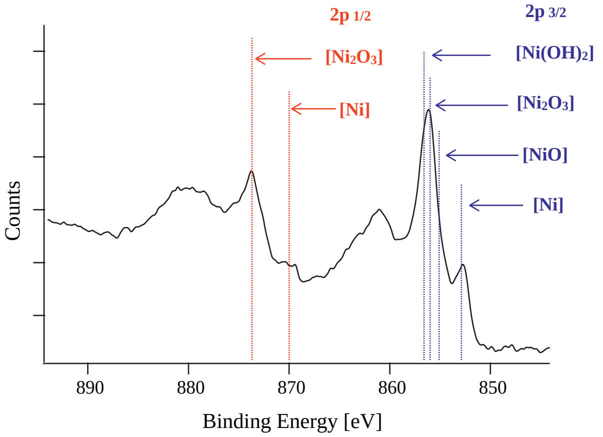

Fig. 1. High resolution XPS spectra of Ni 2p region on NiO nanoparticles prepared by PLD method. The surface was mixture of metallic Ni, nickel oxide and nickel hydroxide.

After the nanoparticles were exposed to air, the chemical state of the NiO particles deposited for 90 s was analyzed by XPS measurement, as shown in Fig. 1. High resolution XPS spectra of Ni 2p region shows shakeup satellite peaks as well as the Ni p$^{1/2}$ and Ni p$^{3/2}$ peaks. The main peak around 855 eV consisted of nickel oxide (Ni^{2}O^3 and NiO) and nickel hydroxide (Ni(OH)^2). Even using an oxide target, Ni 2p$^{3/2}$ peak was revealed at binding energy of 853 eV together with small Ni 2p$^{1/2}$ peak. The nanoparticles were a mixture of metallic Ni, nickel oxide and nickel hydroxide, which agreed with previous studies [7,17]. Interestingly, metal Ni is used as sputtering target in Ref. [7], XPS spectra are almost identical to the one in this study. In either case, the nanoparticles were a mixture of Ni(0), Ni(II) and Ni(III) chemical states.

The SEM image of the nanoparticles deposited on carbon substrates is shown in Fig. 2 together with the surface of carbon as a reference. There was not clear difference even after 90 s nanoparticles deposition (Fig. 2(b)) due to the size of nanpparticles. To observe the size and distribution of nanoparticles, NiO nanoparticles prepared on the silicon substrate were cross-sectioned by focused ion beam (FIB) and prepared for TEM observation. Fig. 3 shows cross section of TEM image of NiO nanoparticles deposited on Si(1 0 0) substrate for 90 s. An amorphous SiO$_2$ layer existed on top of Si(0 0 1) substrate. The dark spots on the amorphous layer correspond to NiO nanoparticles of diameter ~3 nm. These dark spots were scattered over the surface, indicating the NiO nanoparticles individually existed on the surface of Si(0 0 1) after 90 s ablation. As mentioned above, NiO nanoparticles might form a film after ~3 min of PLD deposition. The size of nanoparticles was uniformly ~3 nm, which was comparable to previous studies using PLD [11] and magnetron sputtering methods [7,18].

Cyclic voltammograms were obtained in 0.1 M NaOH solution (dashed line) and in addition 1 mM glucose (solid line) on samples prepared by PLD for 60 and 90 s at the scan rate of 50 mV/s, together with a bulk Ni electrode (black line) as a reference (Fig. 4). The peak currents varied in range of 0.5–0.55 V with the deposition time of NiO nanoparticles, which agreed with previous study using Ag/AgCl as a reference electrode [7]. These peaks in CV measurement was considered to be due to the following reactions of Ni(OH)$_2$:

$$\mathrm{Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O} + e^-, \tag{1}$$

and these peak positions shifted in higher potential. It is known that diamonds prepared by plasma CVD can be used as a working electrode to detect glucose [19,20], however, the peak potential of glucose detection is more than 0.65 V, even with Cu implanted diamond electrode.

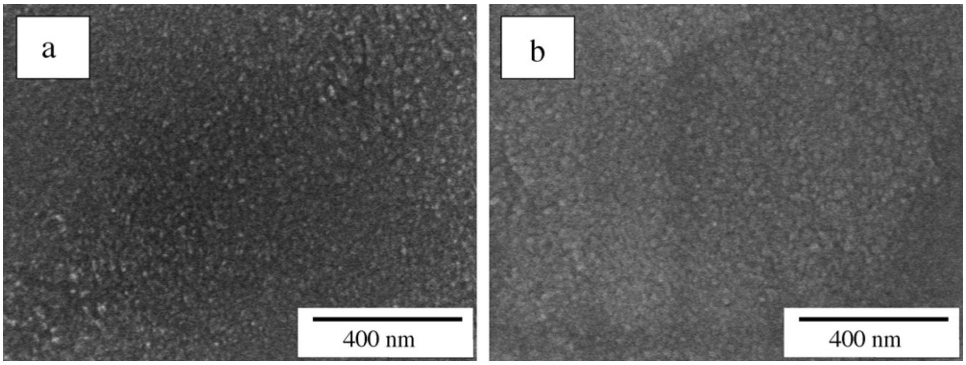

Fig. 2. SEM images of surface of carbon (a) before and (b) after nanoparticles deposition. The nanoparticles were deposited for 90 s on the carbon substrate.

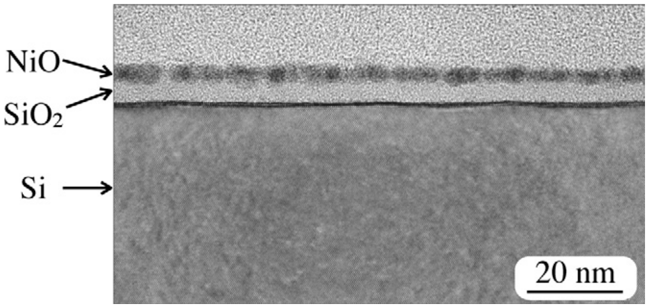

Fig. 3. Cross section of TEM image of NiO nanoparticles deposited on Si(1 0 0) substrate for 90 s. NiO nanoparticles were scattered on on amorphous silicon oxide layer of Si(0 0 1) substrate. The size of NiO nanoparticle was estimated to be ~3 nm.

Fig. 5 shows the summary of peak currents and potential with and without glucose in alkaline media. The solid line with circles (red) shows the differences between peak currents with and without glucose, ΔI_p, and the solid line with circles (blue) shows the differences between potentials (peak-to-peak separation potential ΔE). The dashed lines indicate ΔI_p and ΔE from Ni bulk samples as a reference. NiO nanoparticles used in this study have the advantage of glucose oxidization at lower potential than a diamond electrode.

One of advantage of using the PLD method was easy control of the surface coverage of nanoparticles. The sample with a deposition time of 120 s showed the same properties as Ni bulk samples, indicating the surface was covered with nanoparticles. The surface morphology rapidly became smooth after deposition time of ~90 s.

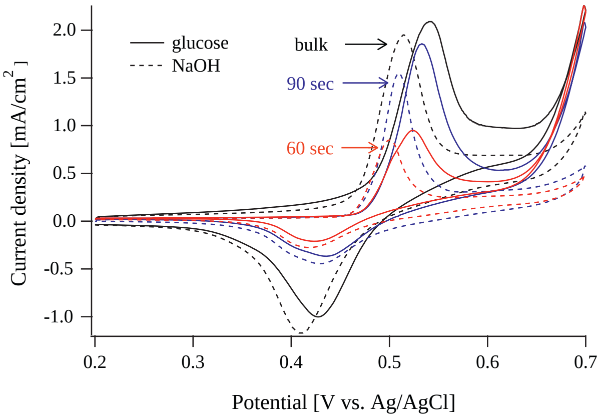

Fig. 4. Cyclic voltammograms were obtained in 0.1 M NaOH solution (dashed line) and in additional 1 mM glucose (solid line) on samples prepared by PLD for 60 and 90 s at the scan rate of 50 mV/s together with a bulk Ni electrode (black line) as a reference.

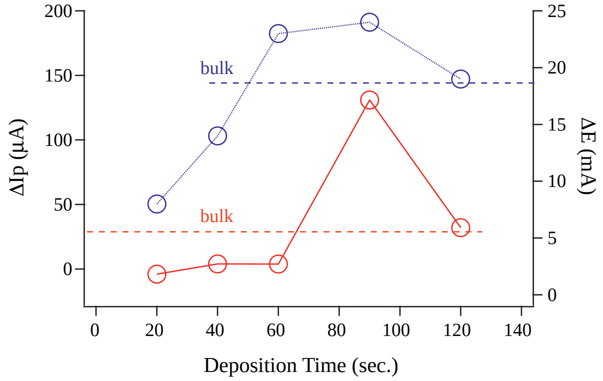

Fig. 5. Summary of peak currents and potential with and without glucose in alkaline media. The solid line with circles (red, bottom) shows the differences between peak currents with and without glucose (ΔI_p), and the solid line with circles (blue, top) shows the differences between potentials (ΔE). The dashed lines indicates ΔI_p and ΔE from Ni bulk samples as a reference. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

While the sample deposited on Si(0 0 1) less than 90 s showed Si peaks on both XPS and AES spectra, the sample deposited for 3 min showed no peaks that originated from Si substrate. After a deposition time of 3 min nanoparticles were covered all the top surface. With an increasing deposition time nanoparticles were scattered all over the surface. The total surface area consisting of nanaoparticles increased until the emergence of two adjacent nanoparticles. With further deposition nanoparticles formed a flat surface and its properties were close to those of bulk samples at deposition time of 120 s as shown in Fig. 5. There existed an optimal coverage for catalyst before the nanoparticles covered all the top surface at deposition time at more than 3 min.

Another advantage of the PLD method, besides the surface coverage of nanoparticles, is that the size of nanoparticles can be controlled by the partial pressure during deposition [11]. The effect of catalyst must be dependent on the size and concentration of nanoparticles on the electrode. Evaluation of nanoparticle size prepared in a variety of partial pressures is in progress.

4. Conclusion

NiO nanoparticles with the size of ~3 nm were deposited on GC substrates by PLD using a Nd YAG laser. Cyclic voltammetry was performed on the samples for electrochemical detection of glucose. The differences between peak currents with and without glucose in alkali media were evaluated to investigate the effect of nanoparticles as a catalyst. There existed optimal coverage for catalyst before the nanoparticles covered the surface of electrode. With increasing surface coverage, nanoparticles formed flat a surface and its properties were closed to those of bulk samples, when the surface was all covered by nanopaticles.

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