Local surface potential measurement of Pd/GaAs contact and anodized aluminum films using scanning probe microscopy

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Abstract. We show that the surface potential measurement using scanning probe microscopy can measure potential distributions of a Pd/GaAs contact and absolute values of the potentials on individual anodized aluminum films. A potential difference was obtained between the Pd film and GaAs substrate, which is close to the barrier height of the same Pd/GaAs contact as estimated from the conventional current–voltage method. For the anodized aluminum films, we clarified that the surface potential varies with surface treatments by measuring absolute values of the potential for individual samples.

1. Introduction

Recently, a new technique has been discovered which maps local surface potential distribution [1–4] together with topography using a scanning probe microscope (SPM), by keeping a certain separation between the sample surface and conductive tip attached on the free end of a cantilever to which a sinusoidal voltage is applied. In case of a difference in potentials between the tip and sample surfaces, an oscillating electromagnetic force appears between the tip and sample surface at the frequency of the applied sinusoidal voltage, which makes the cantilever oscillate [2]. This oscillation is used as the feedback parameter for the system which tries to stop this oscillation by applying a dc voltage to the tip so as to make the potential difference between the tip and sample surfaces vanish. This applied dc voltage to the tip is thus equal to the surface potential of the sample, which makes the surface potential measurable together with the topography.

It is well known that when a metal is contacted with a semiconductor, a potential barrier appears between them which is equal to the difference of the work function of the metal and electron affinity of the semiconductor. The barrier height is usually estimated from changes in electrical current or capacitance when a bias voltage is applied to the interface [5]. A local potential on surfaces consisting of the metal and semiconductor can be used to evaluate the contact potential between the metal and semiconductor. We compared the surface potential difference between the Pd film and GaAs substrate and the barrier height estimated by the conventional current–voltage measurement [5, 6].

The surface potential measurement using SPM is mainly and usually used to map the distribution of potentials on a surface. This is because the distribution of the surface potential is enough to address questions regarding surface phenomena under consideration in many cases [2–4]. However, applications of the surface potential measurement are not limited to measuring potential distribution on a surface. We in fact needed to compare surface potentials on individual samples by measuring their absolute potential values. We note that the technique has the ability to measure absolute values of potential under certain conditions demonstrated with Au films deposited on a glass substrate. We show a comparison of surface potentials measured on individual anodized aluminum films, which are an important substrate for an electronic printing system, treated with phosphoric acid as a function of its concentration. Surface potentials were found to change with the surface treatment, showing that the technique can be used to measure and compare surface potentials for individual surfaces. In this paper we will clarify that absolute values of potential for anodized aluminum films with a well defined reference electrode can be measured, which provides more information for understanding surface phenomena. The difference observed in the surface potential on various samples will be discussed with the residual phosphor as estimated from the x-ray photoelectron spectroscopy (XPS).

2. Experiment

We used a commercial SPM (NanoScope III, Digital Instruments) which is capable of a 'tapping' mode in which the cantilever is oscillated through a bimorph device at around its resonant frequency and the decrease of the oscillation magnitude when the tip approaches the surface is used as the feedback parameter to obtain a topographic image. An 'interleave' scan is performed by lifting the tip up a certain distance (for example, 100 nm) from the local topography obtained with the tapping mode. During the interleave scan, the sinusoidal voltage that is used to oscillate the cantilever through the bimorph during the topographic scan is turned off and switched to connect to the conductive cantilever to make the potential measurable.

A rectangular-shaped silicon cantilever (Nanoprobe) with a tip 10 μm long located at its free end was used in this study. The length, width and thickness of the cantilever are 225, 50 and 2 μm, respectively. The tip apex radius and resonant frequency of the cantilever are about 20 nm and 70 kHz, respectively. We deposited Pt–Pd alloyed particles using the ion-sputtering method onto the cantilever to produce a conductive tip, which typically resulted in an increase in the tip apex radius to 60–100 nm (as evaluated from scanning electron microscopy studies) and a decrease in the resonant frequency to around 50 kHz, respectively. A sinusoidal voltage with a frequency set at the resonant frequency of the cantilever was applied to the bimorph device to oscillate the cantilever to make the cantilever oscillate with an amplitude of 1.5 V (as detected with the photo detector). Topography data were obtained by setting the amplitude kept at about 1.1 V during the tapping mode scan. Surface potentials were measured in the interleave scan with a separation of 100 nm between the tip and local topography during which a sinusoidal voltage with the same frequency and an amplitude of 5 V was applied to the tip directly. All experiments were performed in air ambient at room temperature.

Two separated Au films were deposited onto a glass (oxide of silicon) substrate using the ion-sputtering method, which served as the two electrodes to which we applied dc voltages to produce a 'known' surface potential distribution. This sample was used as a testing device for the surface potential measurement and for a confirmation of the potential of the reference electrode.

Palladium was evaporated in a high vacuum onto an n-type GaAs substrate to form Pd on GaAs Schottky contact dots, whose diameter is 500 μm. The sample was annealed at 250 °C for 15 min. To measure the Pd on GaAs Schottky barrier height using the conventional current-voltage method, an ohmic contact on the back side of the GaAs substrate was formed [6]. The current was measured with an electrometer (Keithley 614). The barrier height was used to test the contact potential difference measured using SPM by scanning the Pd film and GaAs substrate surfaces. The ohmic contact was grounded in the SPM measurement.

An anodized aluminum film was prepared on an aluminum substrate with an area of 8×10 cm^2 in a solution consisting of 30 wt% phosphoric acid and 0.6 wt% sulfuric acid. During the anodization the current density and voltage
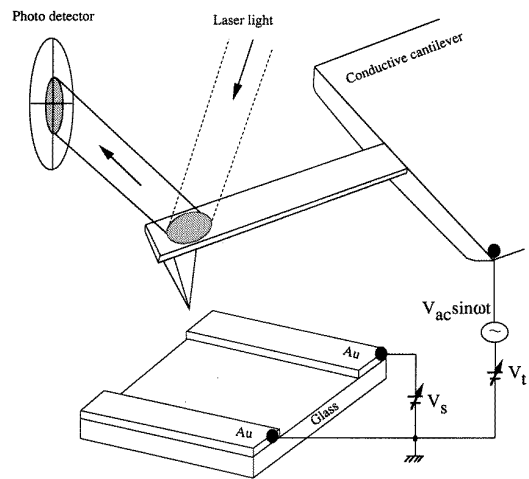

Figure 1. Configuration for the surface potential measurement on a testing sample consisting of two Au films deposited on a glass substrate, one of which is grounded and serves as the reference electrode. A dc voltage (V_s) is applied to the other Au film to produce a known potential to be measured by the scanning probe microscopy with a conductive cantilever. Also shown is a sinusoidal voltage ($V_{ac} \sin \omega t$) used to produce an oscillating force to the cantilever in case of an existence of a potential difference between the tip and sample. The oscillating force is detected by a photo detector with a laser beam reflected from the free end of the cantilever. A dc voltage (V_t) is to be applied to the cantilever to make the potential difference between the tip and sample surfaces vanish.

were kept at 30 mA cm^{-2} and 40 V, respectively, for 120 s. The thickness of the anodized aluminum film was 500 nm. Three samples with an area of 1×1 cm^2 were cut out from the substrate for an experiment aiming to investigate the effect of surface potential change with surface treatments. Two of them were treated by phosphoric acid solutions with concentrations of 2 and 8 wt%, respectively. The third one was washed by deionized water. A qualitative estimation on the amount of the surface phosphor from its 2s peak strength in XPS was used to discuss the observed surface potential changes due to the surface treatments. The x-ray source used in the XPS (Kratos, XSAM-800pci) is Mg $K\alpha$ (1253.6 eV).

3. Results and discussion

We first measured a surface potential distribution that we made by applying a dc voltage to the sample consisting of two separated gold films deposited on a glass substrate. The configuration for the surface potential measurement is shown in figure 1. Providing that a difference of potentials is present between the tip (V_t) and sample surface (V_s), applying a sinusoidal voltage $V_{ac} \sin \omega t$ to the tip induces an oscillating electromagnetic force. The details on the electromagnetic force have been described by Yokoyama and Inoue [2]. By applying an appropriate dc voltage V_t to the tip, the SPM system makes the oscillation of the cantilever vanish. This result indicates that the potential difference between the tip and surface becomes zero, $V_t - V_s = 0$, from which the surface potential V_s is mapped.
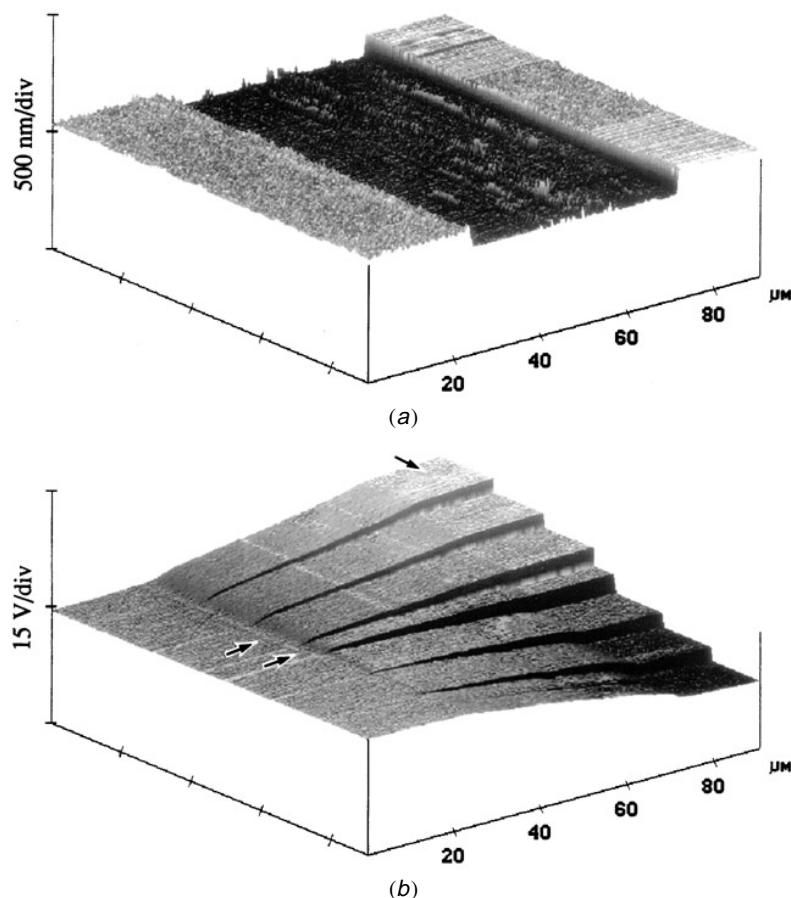
(*a*)

(*b*)

Figure 2. (*a*) Topography and (*b*) surface potential image obtained simultaneously on the testing Au films to which dc voltages are applied to produce known potential distributions as described in figure 1. (*c*) and (*d*) show three profiles of surface potential across the sample at three locations marked by arrows in (*b*). The profile in (*c*) traces the voltage applied to the right-hand side Au film. The two profiles in (*d*) show two potential distributions across the Au films under an applied voltage of 2.3 and 0 V, respectively.

During the scan on the Au film sample for topography and potential distribution image we changed the applied voltage from 5.7 V to −5.7 V gradually with certain intervals. The simultaneously obtained topography and surface potential image are shown in figures 2(*a*) and 2(*b*), respectively. The two Au films serving as electrodes are seen in figure 2(*a*) whose average thickness is 65 nm. As shown in the potential image in figure 2(*b*), on the right-hand side Au film there is a potential distribution corresponding to the applied voltages. On the left-hand side Au film, the reference electrode, the potential does not change with the applied voltage and is kept at 0 V. Figure 2(*b*) also shows that the potential across the glass substrate between the two Au films shows a change from a certain value on the right-hand side to 0 V on the left-hand side. We confirmed that the surface potential distribution shown in figure 2(*b*) was measured to be constant when the separation distance between the tip and sample surface changed from 50 to 3000 nm. This is because the condition for the oscillating force to vanish under consideration is determined by the difference of the surface potentials between the tip and sample surface, although the oscillating force itself changes with the separation distance because the tip–sample capacitance changes with the distance [2]. The

separation distance made a slight change in the potential measurement sensitivity. We checked the sensitivity on a flat Au film as a function of the separation distance and found that the sensitivity remained at 2 mV when the distance increased from 50 to 500 nm. When the separation increased to 1000 and 3000 nm, the sensitivity decreased to 3 and 4 mV, respectively.

Three profiles are obtained for the surface potential across the sample surface at three locations marked by three arrows shown in figure 2(*b*). Figure 2(*c*) shows a profile for the surface potential changing from 5.7 to −5.7 V, which traces the dc voltages that we applied to the right-hand side Au film. In figure 2(*d*), a surface potential profile across the two Au films without applied voltage (0 V) shows that the potential on both Au films is approximately 0 V, while the potential on the glass substrate is 0.3–0.5 V. This potential difference is considered a result of the lowering of the work function [7] of the Au film due to a contact effect with the glass. The work function of gold with respect to the silicon dioxide conduction band obtained with the photoemission technique is 0.6 eV lower than its vacuum work function [8]. This lowering of the work function indicates a formation of a potential barrier for electrons in the conduction band of the oxide. The potential difference
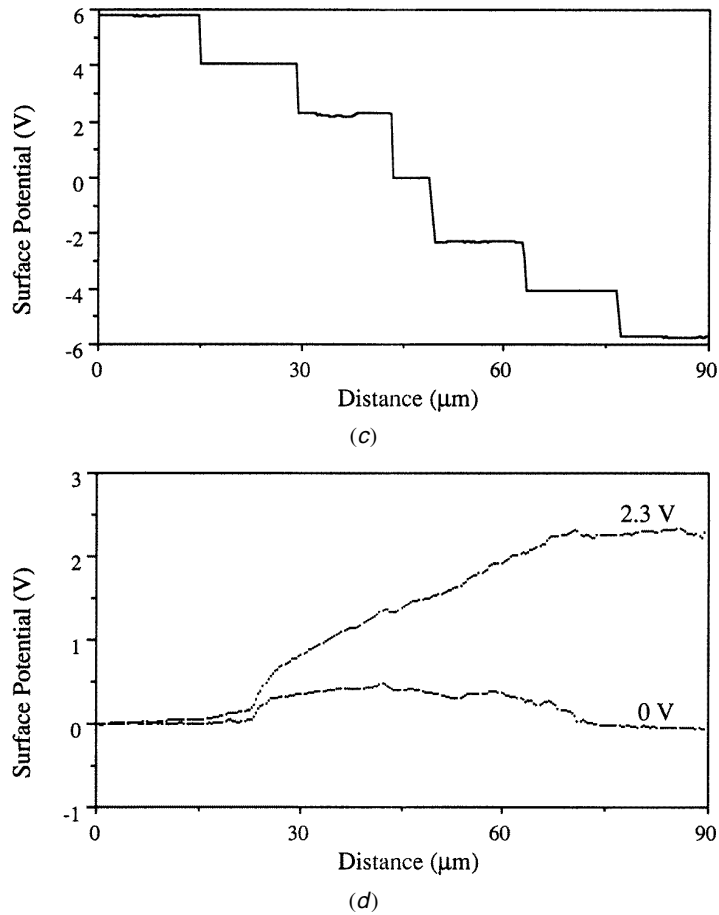
(c)

(d)

Figure 2. (Continued)

of 0.3–0.5 V that we observed between the Au film and glass substrate is consistent with the reported lowering of the work function of gold with respect to the silicon dioxide conduction band [7, 8]. Figure 2(d) also shows the third profile for the surface potential across the two Au films and the glass substrate in between with a voltage of 2.3 V applied to the right-hand side Au film. We can see that the surface potential is 2.3 V on the right-hand side Au film and shows a linear decrease on the glass surface and finally becomes 0 V when arriving at the reference electrode (the left-hand side Au film).

We can see that the surface potential on the reference electrode is almost kept at approximately 0 V. This indicates that the surface potential on the reference electrode is almost the same as that on the tip, which is maintained by the system if they are completely electrical conductors on which there are no effective adsorbates on the surfaces. This is important for comparing potentials for various samples because we have a reference electrode on which the potential is ensured to be absolutely 0 V. It is thus obvious that the surface potential measurement using SPM is capable of detecting not only the distribution of, but also the absolute values of the surface potential. We applied this technique to the Pd on GaAs Schottky contact to measure the contact potential and compare it with the barrier height estimated by the current–voltage method.

We also measured absolute values for surface potentials on individual anodized aluminum films to clarify surface potential changes with surface treatments.

The topography and surface potential distribution image in an area of 165×165 μm^2 on the sample of the Pd film deposited on the GaAs substrate are shown in figures 3(a) and 3(b), respectively. A small part of one of the Pd dots (whose diameter is 500 μm) is shown on the left-hand side of figure 3(a) as the brighter (higher in height difference) part and the rest is the GaAs substrate. The small protrusions seen on both the Pd film and the GaAs substrate are due to surface contamination. The surface potential distribution on the sample surface in figure 3(b) shows that the potential on the Pd film is much lower than that on the GaAs substrate. A profile of the surface potential across the Pd film and GaAs substrate is obtained at a location marked by the arrow in figure 3(b). The profile is shown in figure 3(c) in which the arrow indicates the boundary between the Pd film and GaAs substrate. Note that the potential scale shows the relative difference between the Pd film and GaAs substrate and the insert scale bar is for 0.20 V. As can be seen from the image in figure 3(b) or the profile in figure 3(c) of the potential distribution, the potential across the Pd film and GaAs substrate boundary does not show such a sharp change as that in the topography in figure 3(a). This experimental fact
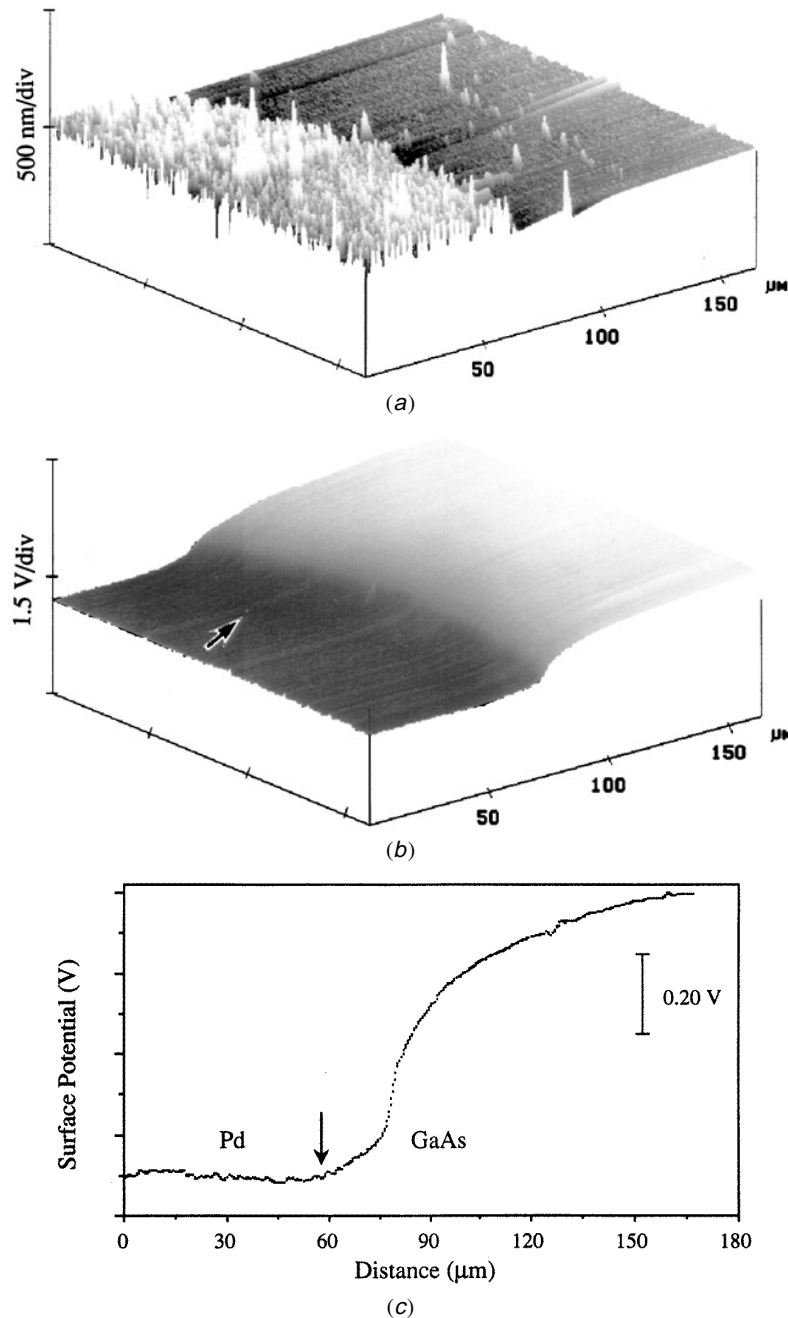
(a)

(b)

(c)

Figure 3. (a) Topography and (b) surface potential image obtained simultaneously on a Pd film deposited on an *n*-type GaAs substrate. A profile of surface potential across the Pd film and GaAs substrate marked by an arrow in (b) is shown in (c).

indicates that the surface potential may have a spreading effect on the GaAs surface around the Pd film. The reason for the shape of the surface potential on the GaAs surface near the Pd film is under investigation.

Potentials on the GaAs substrate surfaces around the Pd film are much lower than those on the GaAs substrate surfaces far away from the Pd film. Although the change in the surface potential distribution on the GaAs substrate around the Pd film shows a complicated behavior, from figure 3(c) we can estimate that the surface potential on the Pd film is 0.72 V lower than that on the GaAs substrate. By changing the separation between the tip and surface from 50 to 3000 nm, we confirmed that the surface potential

difference did not change. With different tips we measured several Pd dots on the same GaAs substrate and found that the contact potential difference changed in the range of 0.58–0.72 V.

For a contact of a metal and an *n*-type semiconductor, the barrier height for the contact interface is $(\varphi_m - \chi - E_f)/e$, where φ_m is the work function of the metal, e is the elementary charge (negative), χ and E_f are the electron affinity and Fermi level of the semiconductor, respectively [5]. According to the reported work function of Pd and electron affinity of GaAs, the contact potential can be calculated to be 1.05 V [6]. For the annealed Pd/GaAs Schottky contact there is a formation of a ternary phase
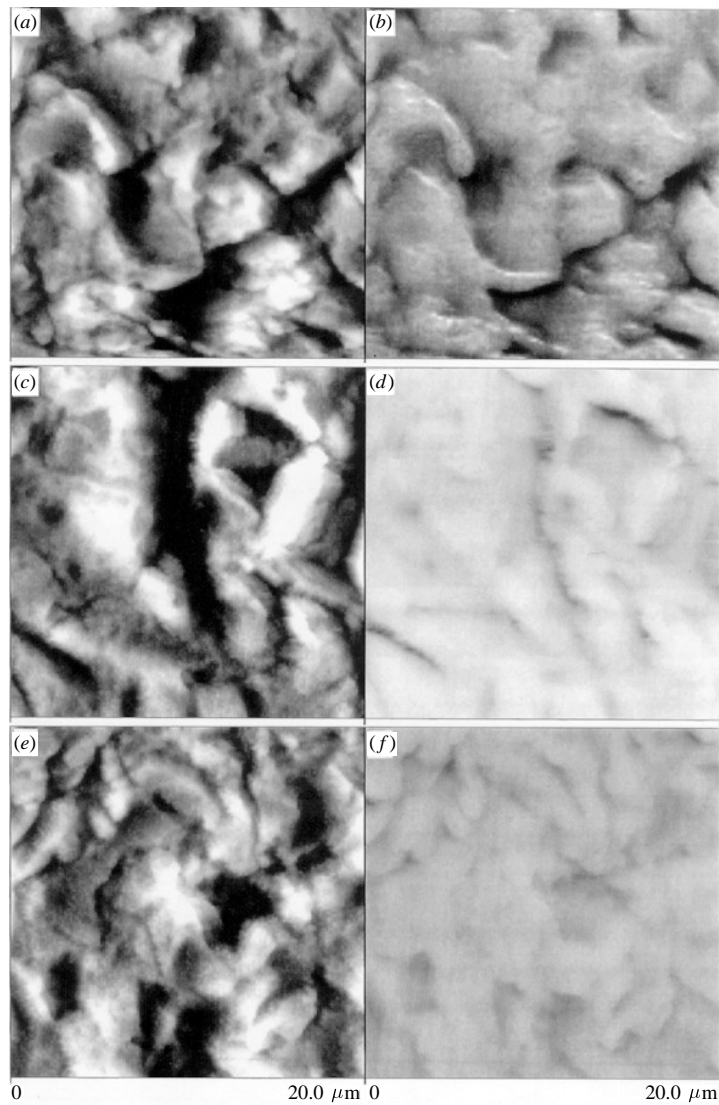
0   20.0 μm   0   20.0 μm

Figure 4. Simultaneously obtained topography (on the left-hand side) and surface potential image (on the right-hand side) on three anodized aluminum films: (*a*) and (*b*) for the water-washed, (*c*) and (*d*) for the 2%, (*e*) and (*f*) for the 8% phosphoric acid solution treated samples, respectively.

of Pd–Ga–As, a metallic compound, at the interface which results in a barrier height of 0.82 eV [6]. For the same Pd dot used for the surface potential measurement as shown in figure 3, we measured the current variation by applying forward bias voltages to the Pd film with respect to the ohmic contact. The intercept at the current density axis is used to evaluate the barrier height. The barrier height estimated from this conventional current–voltage method was 0.81 eV.

The barrier height estimated from the current–voltage method is for electrons to overcome to enter the metal from the GaAs conduction band. This barrier height is determined by the Pd and GaAs interface structure and expected not to be affected by the surface contamination on the Pd film. On the other hand, the contact potential measured by the SPM is the difference of the surface potentials on the Pd film and GaAs substrate surfaces with respect to the reference electrode. By considering surface

effects such as the adsorption effect on the Pd film and GaAs substrate, the value of 0.58–0.72 V for the contact potential is a reasonable value.

We measured topographic and potential images on three samples of the anodized aluminum films treated with deionized water, 2% and 8% phosphoric acid solutions, respectively. Surface potentials for these three samples were measured separately. In order to make these individual measurements comparable with each other, we noted that certain conditions must be fulfilled. We ensured the following two conditions during the potential measurement: (1) using a conductive paste to connect the aluminum substrate electrically to the sample holder that is grounded and serves as the reference electrode; (2) finishing measurements on all samples consequently within 2 h using the same cantilever without any detectable degradation. With the above special caution we consider that only differences related to the anodized film surfaces
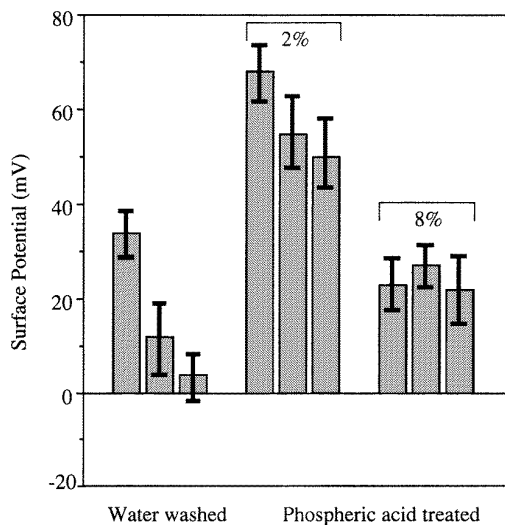
Figure 5. The absolute values (shadow columns) of surface potentials averaged in an area of $20 \times 20 \ \mu m^2$ for the water-washed, 2% and 8% phosphoric acid treated anodized aluminum samples. Also shown are the deviation values (full lines) for the averaged surface potentials.

Figure 6. The phosphorus 2s XPS spectra measured on (*a*) the water-washed, (*b*) 2% and (*c*) 8% phosphoric acid treated anodized aluminum samples.

correspond to the change in the surface potentials. In other words, we can measure relative changes in surface potentials for the three samples.

Local surface potentials at three locations ($20 \times 20 \ \mu m^2$) separated by 50 μm were measured for each sample. We show one set of topography and potential image in figures 4(*a*) and (*b*) for the water washed, figures 4(*c*) and (*d*) for 2% and figures 4(*e*) and (*f*) for 8% phosphoric acid treated samples, respectively. The gray scale for the topographic images is from 0 to 2 μm and the root mean square roughness is about 310 nm for figures 4(*a*), (*c*) and (*e*). Potential images in figures 4(*b*), (*d*) and (*f*) show different absolute values for the surface potential on the three samples. The gray scale is from 0 to 0.1 V in figure 4(*b*) and 0 to 0.3 V in figures 4(*d*) and (*f*), respectively.

As can be seen in figure 4, the potentials measured on the anodized aluminum films are dependent on the surface treatment. The results for the absolute surface potential averaged within the scan areas are shown in figure 5. Also shown are root mean square values for the deviation of the averaged potentials. The potentials measured on the water-washed sample show a large scattering ranging from 34 to 4 mV. The three data for the 2% phosphoric acid treatment show that the surface potentials changed in a relatively small range, from 68 to 50 mV. The data for the 8% phosphoric acid treatment only showed a small change ranging from 22 to 27 mV on the three areas. Although the absolute values of the surface potential for the three samples differ, their distributions are quite similar to each other, as shown in figures 4(*b*), (*d*) and (*f*) and the root mean square values of the deviation for the three potential images range from 10 to 15 mV.

In order to confirm the reproducibility of the trend of the surface potential variation for the phosphoric acid treated surfaces, we measured another set of samples prepared
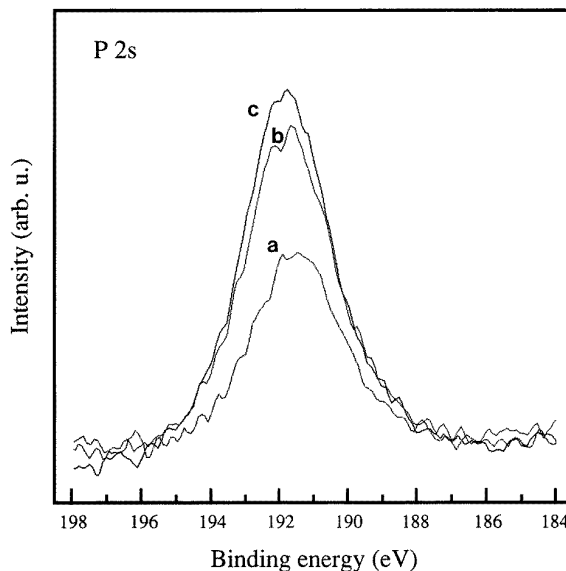
from a different anodized aluminum substrate with the same surface treatment as described above. The difference of the surface potentials between the 2% and 8% phosphoric acid treated films was 30 mV. On the other hand, for the water-washed sample, the surface potential was unstable, which is similar to the data for the water-washed sample shown in figure 5.

There are two notable features in surface potentials shown in figure 5. One is that the phosphoric acid treatment has an effect of stabilizing the surface potential distribution. For the water-washed sample, the surface potentials measured at the three locations changed remarkably. The surface of this kind may be poisoned by many adsorbates such as water films and hydrocarbon. When the phosphoric acid concentration increases the surface potentials measured at three locations became more and more stable. The reason for the stabilization of the surface potential caused by phosphoric acid treatment may be that the phosphoric acid treatment cleans the surface. The other feature in figure 5 is that the surface potential decreases when the phosphoric acid concentration increases.

To investigate the effect of phosphoric acid treatment on the surface potential we measured the amount of phosphor residual on the film surface for the three kinds of treatments. The phosphorus 2s XPS spectra for (a) the water-washed, (b) the 2% and (c) the 8% phosphoric acid solution treatment are shown in figure 6. It is obvious that there is an increase in the strength of the phosphorus 2s peak by the phosphoric acid treatment. This result indicates that the phosphoric acid treatment has an effect to enrich phosphorus on the surface. The phosphorus 2s peak for the water-washed sample is also detected. This is because there is a certain amount of phosphorus in the anodized aluminum film that is prepared in a solution consisting of phosphoric acid.

By comparing the results in figures 5 and 6, for the phosphoric acid treated samples the surface potential

decreases with the increase of phosphorus on the surface. Although the mechanism for the relationship between the residual phosphorus and surface potential remains unclear, we clarified that due to measuring their absolute values, the surface potentials can be used to evaluate the effect of surface treatments. We note that the water-washed sample does not follow this trend and hence consider that surface contamination is in competition with effects caused by the residual phosphorus. The experimental fact that the surface potential measured on the water-washed sample is very unstable can be considered as a side evidence for the surface contamination effect.

4. Conclusions

We demonstrated a local surface potential measurement of known surface potentials produced on Au films and its applications to measure contact potentials between a Pd film and an n-type GaAs substrate and absolute potential values for individual anodized aluminum films.

A potential difference of 0.58–0.72 V between the GaAs substrate and Pd film was measured, which is compatible with the barrier height (0.81 eV) of the same Pd/GaAs contact estimated from the conventional current–voltage method. We clarified that by defining a reference electrode, not only the distribution of, but also the absolute value of, local surface potentials can be measured. Surface potentials corresponding to individual samples were measured and compared with each other for three anodized aluminum films treated with deionized water, 2% and 8% phosphoric acid solutions. Phosphoric acid treatments were found to stabilize the distribution of, and decrease, surface potentials. The ability to measure absolute potential values for the local surface potential technique is considered to enormously enhance its applications in the materials research field as well as in industry.

Acknowledgments

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