Electrochemical Potential Dependence of an Ultrafast Nonequilibrium Electron Dynamics at Au(111) Electrode/Aqueous Solution Interfaces Modified with Alkanethiols

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Femtosecond transient reflectivity measurements were performed for Au(111) electrode/aqueous solution interfaces under electrochemical potential control. Electrode interfaces modified with and without a self-assembled monolayer of alkanethiols were studied in aqueous solutions of $HClO_4$ and H_2SO_4. Dependence on electrochemical potential, interface modification, and kind of solute anions are observed concerning the transient reflectivity response in 3ps. For Au electrodes in an aqueous $HClO_4$ solution, the rate of the initial relaxation at an unmodified interface, $6-10 \ ps^{-1}$, decreased with the electrochemical potential at the potential range where a water dipole rearranged. The rate for alkanethiol-modified interfaces showed a tendency depending on the hydrocarbon chain length. A relative deposited energy from absorbed photon energy was estimated, indicating that interface modification with alkanethiols restricted energy dissipation from the interface. Our trial could contribute not only to develop a study of interaction between a substrate and adsorbed molecules in an ultrafast time scale but also to elucidate elementally processes of electrochemical reactions such as oxidation/reduction reactions at an electrode interface.

Introduction

Recently, spectroscopic measurements using femtosecond lasers have provided important information about electron dynamics in molecules and materials with a time resolution of femtoseconds.[1−3] Ultrafast energy transfer at a solid surface has the potential for significant applications involving noble chemical reactions. For instance, Bonn et al. found that a hot electron mediated catalytic reaction of CO on Ru surface, which could not have been caused by thermal activation.[4] Scientists are interested in the ultrafast relaxation processes of photoexcited electrons in metal, in which the majority of the photon energy is rapidly transformed into heat that is emitted from the photoabsorbing metal surface into the surrounding atoms and molecules. This ultrafast interaction between a substrate and adsorbed molecules can dominate final chemical products and final energy redistribution at an interface after photoillumination.[5]

Spectroscopy for optical transmittance or reflectivity of material reveals the participation of electron motion, which is related to an optical constant as a complex refractive index and, thus, a complex dielectric constant. Optical properties reflect the density of state and the population of electrons in the metal. The probability of a transition between energy states can be observed by measuring reflectivity depending on photon energy, although a relation between the probability and reflectivity has no simple expression for a metal because of the energy-band structure. Spectroscopic measurements with a femtosecond time-scale can observe ultrafast elemental processes of electrons before local thermalization is achieved. Fann et al. have observed an initial electron distribution that does not obey a Fermi−Dirac distribution on a Au surface in a vacuum with a two-photon

photoemission spectroscopy.[1,6,7] Optical excitation by a femtosecond pump pulse creates a non-Fermi distribution of electron gas redistributing to a Fermi distribution through rapid thermalization by electron−electron scattering. Ballistic transport of nonthermalized electrons and diffusive transport of thermalized electrons (called hot electrons) take place. Aeschlimann et al. discussed transport processes of electrons for Au and Ag in a vacuum by using a time-resolved two-photon photoemission technique.[8] The heat is simultaneously transferred from an electronic system to an initially cold lattice by electron−phonon scattering.

Transient reflectivity (TR) measurements are also useful methods for the observation of electron dynamics on metal surfaces.[9,10] Hohlfeld et al. reviewed studies of femtosecond TR and second-harmonic generation (SHG) measurements on metal (Cu, Ag, Au) surfaces in a vacuum.[2,3] Bonn et al. noted the advantages of femtosecond TR measurements by using double-pump pulses on Au, Cu, Cr, and Ru surfaces in a vacuum.[11] Transient reflectivity is also used as a probe to detect the relaxation of an energy state in material after optical excitation by a pump light, in which the assumption that a small change in the dielectric constant is proportional to the extent of small energetic change in the material is generally a good approximation when the reflectivity change is small.

A significant feature of TR measurements is their applicability to a buried interface, for which a two-photon photoemission technique is inadequate. The interfaces of polycrystalline Pt electrodes and Au electrodes have already been studied.[12,13] However, there is little knowledge about the interaction between photoexcited electrons and adsorbed molecules on a metal immerged in a liquid solution. One ideal system for the studies is a colloid solution system of metal nanoparticles because the interfacial area-per-volume fraction of a colloid particle is so large that it is easy to focus on any contribution of interfacial phenomena.[13,14] However, it is not easy to control the electro-

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chemical potential for colloid particles even though the electrochemical potential of metal dominates the chemical and physical states of adsorbed molecules as well as those of surrounding solvent molecules. Apparently, a metal electrode−solution system would be another ideal one for investigating energy transfer across an interface,[13,15] if ultrafast phenomena intrinsic to the interface could be measured under less advantageous conditions than those of colloid solutions. However, little research exists on this subject.

In this paper, using femtosecond TR measurements under an electrochemical potential control, we examine whether ultrafast electron relaxation at well-defined interfaces of a single crystalline Au(111) electrode in aqueous solutions depends on the electrochemical potential and interfacial molecular structure of an adsorbed chemical species. The Au(111) electrode is modified with alkanethiols that have different CH_2-chain lengths and are immerged in aqueous solutions of $HClO_4$ or H_2SO_4. Alkanethiol forms a self-assembled monolayer (SAM) on a Au surface with a Au−S chemical bond. Numerical research concerning the characteristics and molecular structure of SAM on a Au surface has been performed.[16−19] A series of rate constants of the ultrafast decay of transient reflectivity in 3ps with different electrochemical potentials is determined for discussion in connection with the structures of adsorbed molecules on each interface. Relative deposited energy from absorbed photon energy is estimated to discuss the influence of an interface modification on the relaxation of nonequilibrium electrons.

Experimental Section

The experimental setup was the same as the one previously reported.[20] Pump and probe beams were emitted from a mode-locked Ti-sapphire laser. The probe beam had a pulse width of 80 fs (full width at half-maximum of autocorrelation), a wavelength of 800 nm (1.6 eV), and a repetition rate of 81 MHz, and it was passed through an optical delay line. The pump beam was intensity-modulated at 1.4 MHz, and its wavelength was transformed into a second harmonic wave at 400 nm (3.1 eV). The two beams were coaxially combined and focused with a microscope objective lens (magnification, 10; numerical aperture, 0.25) and normally directed into an electrochemical interface. The powers of the pump-and-probe beams were less than 160 and 300 pJ/pulse at the interface, respectively. The reflected probe beam from the interface was detected by a photodiode, and its output signal was fed into a lock-in amplifier. The in-phase signal of the lock-in amplifier was recorded against a delay time of the probe pulse with respect to the pump pulse, which gave a TR response for further processing. Each measured TR response consisted of 600 data points for a 4-ps window of time starting at 0.8 ps before the pump-pulse illumination. A typical TR response is shown in Figure 1 for a Au(111) interface in a 0.1 M $HClO_4$ aqueous solution.

A quartz cell was used for the electrochemical cell. The electrochemical cell consisted of a three-electrode configuration. A hemisphere electrode of a single crystalline Au having a (111)-index surface was laboratory-made using Clavilier's method and served as a working electrode.[21] Two Pt wires were references and counter electrodes. The Pt reference electrode had an electrochemical potential of 0.7 V higher than a standard hydrogen electrode. It was used as a substitution for a generally used reference electrode (i.e., saturated calomel or a Ag/AgCl electrode) to avoid disturbing contamination by Cl⁻. A solution in the electrochemical cell was bubbled with Ar gas to deoxygenate and to preserve the cleanliness of the interface during the experiment.
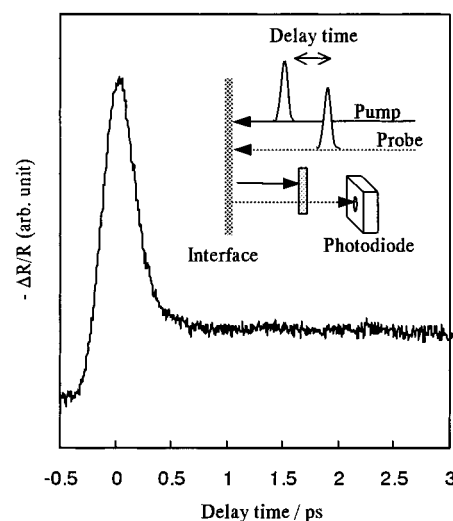

Figure 1. Typical transient reflectivity response of Au(111) in a 0.1 M $HClO_4$ aqueous solution. The inset shows the experimental pump-probe setup; pump: 400 nm; probe: 800 nm; coaxial pump-and-probe beams are introduced normal to the interface.

$HClO_4$ and H_2SO_4 were purchased from Kishida Reagents Chemicals and were used without further purification as a solute electrolyte of aqueous solutions after dilution. Pure water with 18.2 MΩcm was systematically prepared by filtration of Milli-Q filter (Millipore System, Japan Millipore Co., Inc.). 1-octanethiol (OT, $CH_3(CH_2)_7SH$), 1-dodecanethiol (DDT, $CH_3(CH_2)_{11}SH$), and 1-hexadecanethiol (HDT, $CH_3(CH_2)_{15}SH$) were purchased from Tokyo Kasei Kogyo Co., Ltd. and were used without further purification. An alkanethiol adlayer on Au(111) was prepared by immersing a Au electrode in 1 mM alkanethiol ethanolic solution for more than 24 h. All experiments were performed at room temperature in atmospheric pressure.

Results and Discussion

Electrochemical Measurements. A cyclic voltammogram for the unmodified Au(111) interface in a 0.1 M $HClO_4$ aqueous solution shows two oxidation peaks owing to a Au hydroxide and oxide formation at 0.5 and 0.75 V versus Pt in the anodic sweep and one reduction peak at 0.3 V versus Pt in the cathodic sweep.[20] They feature a (111) index surface of Au in a $HClO_4$ aqueous solution.[22] When Au electrodes are modified with alkanethiols, the oxidation and reduction peaks disappear. The electrochemical inertness of the interfaces modified with the alkanethiol adlayers is confirmed for all of the modified Au electrodes used. It is suggested that there are a few water molecules near the modified interfaces because of the hydrophobic environments.

Calculation of Rate Constants for Reflectivity Relaxation and Relative Deposited Energy from Absorbed Photon Energy. Changes in TR responses against different electrochemical potentials and different interfacial structures are small, as described later. We have applied a fitting procedure for each TR response to deduce the characteristic parameters. A time variation of a true TR, $R(t)$, is expressed as

$$R(t) = \Sigma C_i \cdot \exp(-k_i t) + D + \delta(t) \tag{1}$$

where C_i and k_i are the preexponential factors and the decay-rate constant of component i, respectively. D and $\delta(t)$ represent a constant offset to which a slowly decaying component is approximated and an instantly responding component, respectively. To take the laser-pulse duration into account, $R(t)$ is
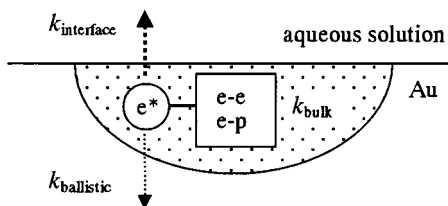
Figure 2. A schematic illustration representing three relaxation pathways of nonequilibrium electrons. Three decay-rate constants compose the total decay-rate constant k: the ballistic transport of nonthermalized electrons into a deep bulk phase or outside the photoilluminated region as $k_{ballistic}$; the electron−electron (e−e) scattering of nonthermalized electrons and electron−phonon (e−p) scattering of thermalized electrons in bulk metal near the interface as k_{bulk}; and the diffusive transport of electronic energy into the aqueous solution side of the interface as $k_{interface}$.

convoluted with the pump-pulse intensity profile $I_{pump}(t)$ and the probe-pulse intensity profile $I_{probe}(t)$, for which Gaussian pulse shapes are assumed. Thus, the $S(t)$ of the fitting function is given by

$$S(t) = \int_{-\infty}^{\infty} I_{probe}(t' - t) \times [\int_{-\infty}^{t'} I_{pump}(t'')R(t' - t'')dt'']dt' \quad (2)$$

Parameters are obtained by analysis with eq 2 for each TR response. Analysis of TR response is performed after normalization of TR response upon the maximum value of a TR intensity to exclude the difference of each experimental condition. We have found that a single-exponential function with D and $\delta(t)$ provided good fitting results for all of the measured TR responses, as it did for those reported previously.[20] The determined decay-rate constants, k, are in a subpicosecond time scale. Although a simple relation has not been found between the TR change and the energy distribution of electrons in a photoexcited metal surface, the relaxation expressed as $\exp(-kt)$ is a theoretically rough but an experimentally good approximation for a state-averaged relaxation of the photoexcited electrons.[1]

When we take into account electronic relaxation processes at the metal interface after illumination of a femtosecond pulse, we can assume that three types of different relaxation at the metal/aqueous solution interface contribute to the decay-rate constant k (Figure 2): $k_{ballistic}$, k_{bulk}, and $k_{interface}$. $k_{ballistic}$ is ballistic transport of nonthermalized electrons into a deep bulk phase or outside the photoilluminated region. k_{bulk} is a relaxation by both electron−electron (e−e) scattering of nonthermalized electrons and electron−phonon (e−p) scattering of thermalized electrons in bulk metal near the interface. $k_{interface}$ is diffusive transport of electronic energy into the aqueous solution side of the interface. Thus, a subpicosecond time scale of the relaxation with the decay-rate constant k comes from all of the relaxation of nonthermalized and thermalized electrons at the interface.[2,3,9,10] A total of the three decay-rate constants is equivalent to the decay-rate constant k.

The constant D is considered to represent a reflectivity change caused by a photoinduced temperature rise after a local equilibrium is achieved between the electron and lattice phonon of the metal interface. A relaxation of the phonon, caused by heat diffusion, would take place in a long time scale (more than 1 ns) so that its contribution to a TR response is well approximated as a constant within the present experimental time scale. The width of a cross-correlation of the pump-and-probe beams is estimated in the same fitting procedure and is 240 fs of a full width at half-maximum. This is caused by pulse stretching in the focusing lens and in the liquid solution. The width is comparable with decay-rate constants of hundreds of

femtoseconds but is small enough to determine decay-rate constants of hundreds of femtoseconds. The $\delta(t)$ term in eq 1 can be expressed by an exponential function with a time constant as small as 20 fs, representing an ultrafast electron dynamic caused by electron−electron scatterings, but we think it responds instantly because of the limited time resolution of our system.

To discuss ultrafast energy dissipation from the photoexcited local region, $R(t = \infty)/R(t = 0)$ equal to $D/(C + D + 1)$ is evaluated with parameters obtained in the fitting procedure. This value represents a relative deposited energy from an absorbed photon energy after a local thermal equilibrium between electrons and phonons is achieved at the interface. When the local equilibrium is fully achieved a few picoseconds after photoexcitation, a small TR change is proportional to the local temperature rise, estimated to be less than 10 K of the photoexcited metal surface. The temperature rise is proportional to D, and it is possible to calibrate D into the temperature rise with a data table of reflectivity at a variety of temperatures. There may be a different way for the nonequilibrium electron to contribute to the TR change, but a linear relation can be assumed between an absorbed energy by the metal and a TR change just after a pump pulse hits the metal interface because it was experimentally confirmed that the pump energy was proportional to the TR signal intensity under the present experimental condition. The $R(t = \infty)/R(t = 0)$ value represents a ratio of the local equilibrium temperature with respect to the amount of absorbed energy. Namely, $R(t = \infty)/R(t = 0)$ can be treated as a measure of the relative deposited energy at the interface. Although the intensities of each TR at the different interfaces are not often the same even for identical intensities of pump-and-probe beams because of different experimental conditions, $R(t = \infty)/R(t = 0)$ each can be compared with the others at the different interfaces by the normalization procedure of TR response before the analysis.

The values of k and $R(t = \infty)/R(t = 0)$, determined against electrochemical potential and different molecular structure at the Au(111) interface, will be discussed in the following section.

Au in an Aqueous HClO4 Solution. Our group has reported that the time constants of TR depended on the electrochemical potential at the Au(111) interface in a 0.1 M aqueous HClO$_4$ solution.[20] We have considered that electrochemical potential dependence is due to the rearrangement of a water dipole that occurs around 0.2 V at the Au(111) interface. Figure 3 represents the potential dependence of a TR response between an electrochemical potential of 0 and 0.3 V versus Pt at the Au(111) interface in an aqueous HClO$_4$ solution. For a good comparison, a fitting result of a TR response at 0 V versus Pt is shown as a solid line. Dots represent the TR response measured at 0.3 V versus Pt. A trace in the lower part is calculated to clearly show the difference between the fitting results at 0 V versus Pt and the measured data at 0.3 V versus Pt. The differences between the TR responses at 0 and 0.3 V versus Pt are quite small, but they can be distinguished from the trace, especially around 0.5 ps of delay time. The calculated values of a decay-rate constant k are 11 ps^{-1} at 0 V versus Pt and 6.6 ps^{-1} at 0.3 V versus Pt, respectively.

When the Au(111) interface is modified with alkanethiols, the rate constants decrease. Figure 4 represents the modification effects of a TR response with OT at 0 V versus Pt in an aqueous HClO$_4$ solution. A fitting result of a TR response at the unmodified Au(111) interface is shown as a solid line. Dots represent a TR response measured at the OT-modified Au(111) interface. A trace representing the difference between them is shown in the lower part. A change by modification is clearly observed at the delay time around 0.5 ps. In fact, a decay-rate
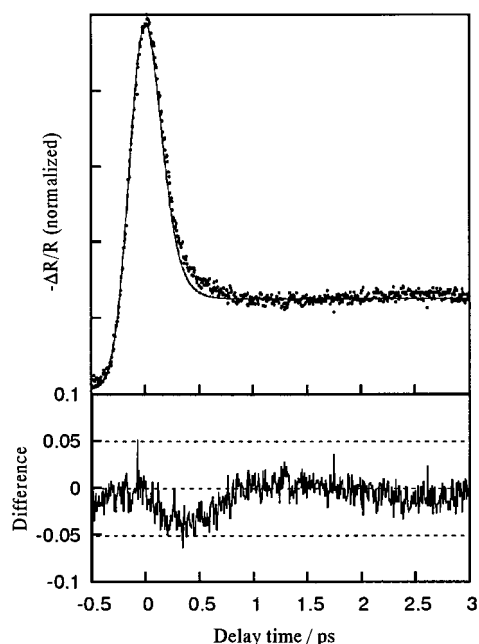
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Figure 3. Upper: a transient reflectivity response at 0.3 V vs Pt (dot) and a fitting line at 0 V vs Pt (solid line) at the unmodified Au(111) interface in a 0.1 M aqueous HClO$_4$ solution. All data are normalized. Lower: difference between them.
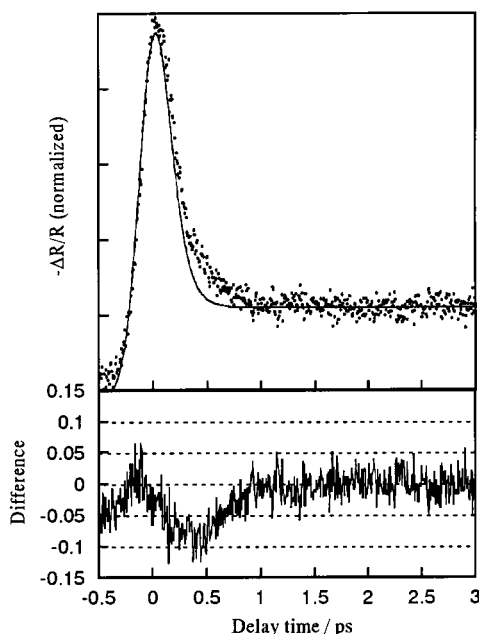

Figure 4. Upper: a transient reflectivity response at the 1-octanethiol modified Au(111) interface (dot) and a fitting line at the unmodified Au(111) interface (solid line) in a 0.1 M aqueous HClO$_4$ solution. The electrochemical potential is 0 V vs Pt. All data are normalized. Lower: difference between them.

constant (4.2 ps^{-1}) at the OT-modified interface is smaller than that at the unmodified interface.

A series of decay-rate constants determined against the electrode potential at the Au(111) interface and a modified one with an OT in an aqueous HClO$_4$ solution is shown in Figure 5 as open and closed circles, respectively. At the unmodified interface, the decay-rate constant k shows clear potential dependence. The dependence of k below 0.4 V versus Pt is due to the water-dipole rearrangement.[20] The rate constants in a potential range above 0.4 V versus Pt (indicated as (a) region in Figure 5) suffer from another contribution different from the
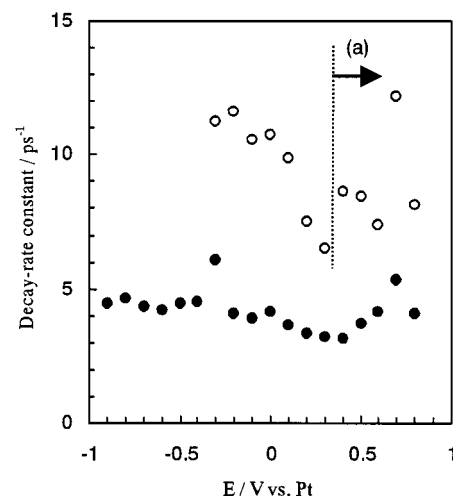

Figure 5. Decay-rate constants at the Au(111) interfaces (open circle) and 1-octanethiol modified Au(111) interface (closed circle) in a 0.1 M aqueous HClO$_4$ solution. (a) indicates an electrochemical potential region where hydroxide and oxide are formed on the unmodified interface.
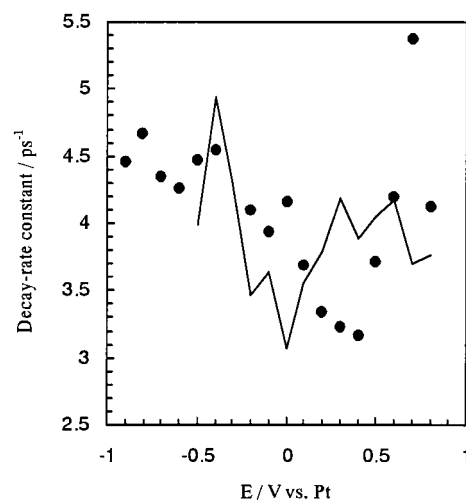

Figure 6. Decay-rate constants (scale magnified) at the 1-octanethiol (closed circle) and 1-hexadecanethiol (solid line) modified Au(111) interfaces in a 0.1 M aqueous HClO$_4$ solution.

water-dipole rearrangement because hydroxide or oxide is formed on the Au(111) interface. Electron dynamics in a photoabsorbing layer of Au oxide should be taken into account.

It is obvious that, through the potential range investigated, the decay-rate constants for the OT-modified interface are smaller than those for the unmodified interface. Averaged values of the decay-rate constants are 9.4 ps^{-1} at the unmodified interface in a measured potential range of −0.3 to 0.8 V versus Pt and 4.2 ps^{-1} at the OT-modified interface in a measured potential range of −0.9 to 0.8 V versus Pt, respectively. Apparently, interface modification reduces the potential dependence of the decay-rate constants. Results of the modification with alkanethiols suggest that the interaction between nonequilibrium electrons in Au and the surrounding environments should be reduced. The potential dependence of the decay-rate constant at the OT-modified interface can still be observed.

Scale-magnified decay-rate constants at the OT-modified interface are shown with those at an HDT-modified interface in Figure 6. At the modified interfaces with alkanethiols, the time scales of the decay-rate constants nearly overlap. Furthermore, the different CH$_2$ chain lengths of alkanethiol may give different potential regions where the decay-rate constants depend
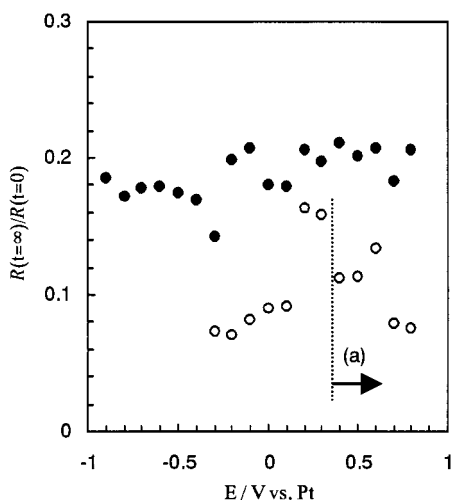
Figure 7. Relative deposited energy from absorbed photon energy at the Au(111) interfaces (open circle) and the 1-octanethiol modified Au(111) interface (closed circle) in a 0.1 M aqueous $HClO_4$ solution. (a) indicates an electrochemical potential region where hydroxide and oxide are formed on the unmodified interface.
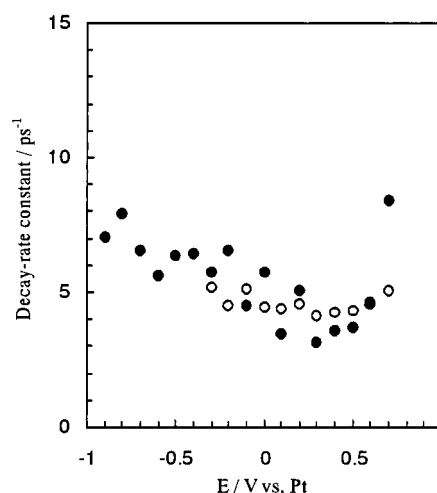

Figure 8. Decay-rate constants at the Au(111) interface (open circle) and the 1-octanethiol modified Au(111) interface (closed circle) in a 0.1 M aqueous H_2SO_4 solution.

on the electrochemical potential. In other words, a dependent potential region depends on the CH_2 chain lengths of alkanethiols at the modified interfaces. Observations indicate that the potential region has a tendency to shift negatively when the CH_2 chain lengths of alkanethiols are increased because the potential region where the decay-rate constant depends on the electrochemical potential at a DDT-modified interface exists between those at OT-modified and HDT-modified interfaces. This occurs because of the existence of a potential region between those at OT-modified and HDT-modified interfaces where the decay-rate constant depends on the electrochemical potential at a DDT-modified interface.

Let us discuss the potential dependence of the decay-rate constants. Three decay-rate constants ($k_{ballistic}$, k_{bulk}, $k_{interface}$) can contribute to the potential dependence of the total decay-rate constant but with different weights. The fact that surface modification causes a large decrease in k indicates that $k_{interface}$ makes a significant contribution. It seems natural to assume that $k_{interface}$ has a potential dependence because the molecular structure at the solution side of the interface (orientation of molecular dipoles and density of adsorbed ions) strongly depends on the electrochemical potential. The nonequilibrium electrons will relax via interaction with molecules near the interface. The k_{bulk} term can be potentially dependent because the electron density concerns the rate constants of electron–electron and electron–phonon scatterings, and the interface electron density is potentially dependent. However, the small potential dependence of k for the modified interface suggests that the contribution of k_{bulk} is not large because, even for the modified interface, an electron density effect similar to that of an unmodified interface would be expected. The $k_{ballistic}$ term would be expected to have a small effect, for the same reason as the k_{bulk} term. This could be significant if the interface-parallel motions of the nonequilibrium electrons were important, but we do not think this possibility is likely because the size of the spot of the pump-laser beam (3 μm) is larger than the mean free path of electrons (10^2 nm) in Au.[2,3]

Figure 7 shows $R(t = \infty)/R(t = 0)$ values against the electrochemical potential at the interfaces in a 0.1 M $HClO_4$ aqueous solution. The $R(t = \infty)/R(t = 0)$ values at the OT-modified interface take larger values than those at the unmodified interface over a potential range of -0.3 to 0.8 V versus Pt. The average values of $R(t = \infty)/R(t = 0)$ are 0.10 for the

unmodified interface in a measured potential range of -0.3 to 0.8 V versus Pt and 0.19 for the OT-modified interface in a measured potential range of -0.9 to 0.8 V versus Pt, respectively. At the unmodified interface, the $R(t = \infty)/R(t = 0)$ values depend on the electrochemical potential and increase at the same potential range where the decay-rate constants decrease, while the $R(t = \infty)/R(t = 0)$ values tend to increase mildly as the electrochemical potential increases at the OT-modified interface. Small values of $R(t = \infty)/R(t = 0)$ for an unmodified interface indicate the high efficiency of energy dissipation from the photoilluminated region.

The reflectivity change caused by photoinduced nonequilibrium electrons is considered to relax by transport of the electrons ($k_{ballistic}$ and $k_{interface}$ terms), electron–electron and electron–phonon scatterings (k_{bulk} term) at the photoilluminated interface. We consider that the phenomena that are responsible for large $R(t = \infty)/R(t = 0)$ values are both the suppression of the transport and the promotion of the electron–electron and electron–phonon scattering. The fact that an interface modification with alkanethiols makes the rate constant small and an $R(t = \infty)/R(t = 0)$ value large is consistent if there is a stronger interaction between water molecules and nonequilibrium electrons than there is between alkanethiol molecules and the electrons. Namely, a larger number of nonequilibrium electrons relaxing in the bulk metal result in a larger increase of temperature in the photoilluminated region at the interface under the local equilibrium condition 1 ps after the pump-pulse illumination.

Our group has previously proposed that an electron transfer and a back transfer between the metal and molecules through the interface take place.[20] We believe that the results of this present analysis support our proposal because the modification by alkanethiols suggests that there is a restriction of the interaction between photoinduced nonequilibrium electrons and water molecules on the aqueous solution side of the interface. On the other hand, the dependencies of the electrochemical potential and CH_2 chain length at the modified interfaces are very interesting. As our research continues, we expect to discover novel chemical processes in an ultrafast time scale.

Au in an Aqueous H2SO4 Solution. A series of decay-rate constants against the electrode potential at the Au(111) interface modified with and without OT in a 0.1 M H_2SO_4 aqueous solution is shown in Figure 8. The decay-rate constants show a similar tendency for both systems regardless of surface modification, as in previous results for DDT- or HDT-modified
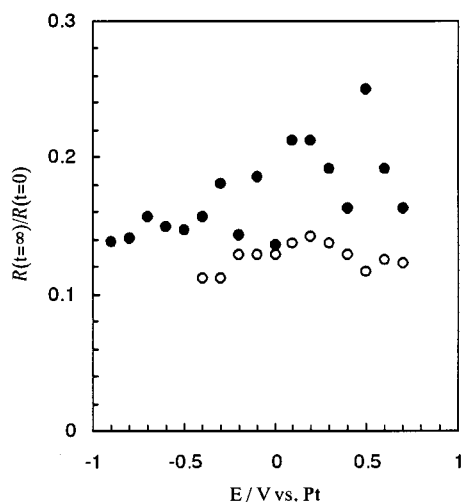
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Figure 9. Relative deposited energy from absorbed photon energy at the Au(111) interfaces (open circle) and the 1-octanethiol modified Au(111) interface (closed circle) in a 0.1 M aqueous H_2SO_4 solution.

interfaces.[20] The average values of the decay-rate constants were 4.6 ps^{-1} at the unmodified interface in a measured potential range of -0.3 to 0.7 V and 5.6 ps^{-1} at the OT-modified interface in a measured potential range of -0.9 to 0.7 V, respectively. The potential dependence of the rate constants is also observed at the unmodified interface; however, the extent of the potential dependence is smaller than those of the Au(111) interface in an $HClO_4$ aqueous solution. The potential ranges where the rate constants take small values show no substantial change by interfacial modification. These results suggest that rate constants are dominated by SO_4^{2-} anions even for the modified Au(111) interfaces although the adlayer might block anions.

Figure 9 shows $R(t = \infty)/R(t = 0)$ values at the Au(111) interface with a different modification in a 0.1 M H_2SO_4 aqueous solution. The average values of the $R(t = \infty)/R(t = 0)$ values are 0.13 at the unmodified interface in a measured potential range of -0.3 to 0.7 V and 0.17 at the OT-modified interface in a measured potential range of -0.9 to 0.7 V, respectively. No drastic change as a result of modification was observed, unlike the results for the system using an aqueous $HClO_4$ solution. However, $R(t = \infty)/R(t = 0)$ at the unmodified interface has a smaller value than that of the modified interface.

It is considered that difference between solutions comes from a different interfacial molecular structure because of the affinity of the anions. The affinity of ClO_4^- for Au is relatively small so that a water molecule can easily approach the interface and rearrange its dipole against the electrochemical potential. On the other hand, a SO_4^{2-} anion with a strong affinity for Au may occupy most of the interface and be inflexible because of the strong interaction. Moreover, we suspect that the strong affinity of SO_4^{2-} allows it to penetrate into the alkanethiol adlayer and be close to the Au interface.

Conclusion

Ultrafast TR responses within 3 ps have been examined against the electrochemical potential at the well-defined Au(111) interfaces modified with and without a self-assembled monolayer of 1-octanethiol in aqueous solutions of $HClO_4$ or H_2SO_4. The decay-rate constants of the TR responses and fraction of light-induced local heating are calculated by a fitting procedure in which three terms (single-exponential decaying, long-lived, and instantly responding terms) are assumed to express the relaxation of a photoinduced reflectivity change.

The decay-rate constants at the OT-modified interface in an $HClO_4$ aqueous solution have smaller values on average than those at the unmodified Au(111) interface. When an H_2SO_4 solution was used, no substantial modification effect was observed, while the rate constants depended on the potential. The dependence of a decay-rate constant is attributed to the diffusive transport of electronic energy into the aqueous solution side of the interface. The estimation of relative deposited energy from absorbed photon energy suggested that a modification of alkanethiols relatively restricts the relaxation of nonequilibrium electrons on the solution side of an interface in an aqueous $HClO_4$ solution. Furthermore, the dependencies of the electro-chemical potential and CH_2 chain length of alkanethiol are suggested.

Our trial could contribute not only to develop a study of interaction between a substrate and adsorbed molecules in an ultrafast time scale but also to elucidate elementally processes of electrochemical reactions such as oxidation/reduction reactions at an electrode interface. Furthermore, knowledge obtained from this study could contribute to the understanding and control of the ultrafast energy flow on a molecular scale. Controlling the ultrafast energy flow, for instance, by surface modification may provide novel chemical reaction pathways at the interface.

References and Notes

(1) Boker, J.; Fann, W. S. *Laser Spectroscopy and photochemistry on metal surfaces part 1*; Advanced Series in Physical Chemistry, Vol. 5; World Scientific: Singapore, 1995; Chapter 8.

(2) Hohlfeld, J.; Wellershoff, S.-S.; Güdde, J.; Corrad, U.; Jähnke, V.; Matthias, E. *Chem. Phys.* **2000**, *251*, 237.

(3) Hohlfeld, J.; Conrad, U.; Muller, J. G.; Wellershoff, S.-S.; Matthias, E. *Nonlinear Optics in Metals*; Clarendon Press: New York, 1998; Chapter 3.

(4) Bonn, M.; Funk, S.; Hess, Ch.; Denzler, D. N.; Stampfl, C.; Scheffler, M.; Wolf, M.; Ertl, G. *Science* **1999**, *285*, 1042.

(5) Wolf, M. *Surf. Sci.* **1997**, *377–379*, 343.

(6) Fann, W. S.; Storz, R.; Tom, H. W. K.; Boker, J. *Phys. Rev. B* **1992**, *46*, 13592.

(7) Fann, W. S.; Storz, R.; Tom, H. W. K.; Boker, J. *Phys. Rev. Let.* **1992**, *68*, 2834.

(8) Aeschlimann, M.; Bauer, M.; Pawlik, S.; Knorren, R.; Bouserar, G.; Bennemann, K. H. *Appl. Phys. A* **2000**, *71*, 485.

(9) Sun, C.-K.; Vallee, F.; Acioli, L.; Ippen, E. P.; Fujimoto, J. K. *Phys. Rev. B* **1993**, *48*, 12365.

(10) Sun, C.-K.; Vallee, F.; Acioli, L.; Ippen, E. P.; Fujimoto, J. K. *Phys. Rev. B* **1994**, *50*, 15337.

(11) Bonn, M.; Denzler, D. N.; Funk, S.; Wolf, M.; Wellershoff, S.-S.; Hohlfeld, J. *Phys. Rev. B* **2000**, *61*, 1101.

(12) Hibara, A.; Harata, A.; Sawada, T. *Chem. Phys. Lett.* **1997**, *272*, 1.

(13) Harata, A.; Shen, Q.; Sawada, T. *Annu. Rev. Phys. Chem.* **1999**, *50*, 193.

(14) Harata, A.; Taura, J.; Ogawa, T. *Jpn. J. Appl. Phys.* **2000**, *39*, 2909.

(15) Harata, A.; Edo, T.; Sawada, T. *Chem. Phys. Lett.* **1996**, *249*, 112.

(16) *Self-Assembled Monolayers of Thiols;* Ulman, A., Ed.; Academic Press: London, 1998.

(17) Sellers, H.; Ulman, A.; Shnidman, Y.; Eilers, J. E. *J. Am. Chem. 1993*, *115*, 9389.

(18) Teran Arce, F.; Vela, M. E.; Salvarezza, R. C.; Arvia, A. J. *Electrochim. Acta* **1998**, *44*, 1053.

(19) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437.

(20) Sugiyama, T.; Ishioka, T.; Harata, A. *Anal. Sci.* **2001**, *17*, s237.

(21) Clavilier, J. J. *Electroanal. Chem.* **1980**, *107*, 211.

(22) Hamelin, A. *J. Electroanal. Chem.* **1996**, *407*, 1.