Bias-voltage induced surface reaction of para-nitrobenzoic acid adsorbed on Ag/AlO_{x}/Al tunnel junction

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Abstract. Surface-enhanced Raman scattering (SERS) spectra of para-nitrobenzoic acid (PNBA) adsorbed on the Ag electrodes of Ag/AlO_{x}/Al tunnel junctions fabricated on plain and CaF_{2}-covered glass substrates are measured under bias-voltage applications. The SERS bands caused by the adsorbed PNBA on the Ag electrode increase in intensity with positive bias-voltage and a new band attributable to the azo-group emerges at voltages greater than +2.2 eV. In contrast, the bands remain nearly unaltered under negative bias-voltage. The intensity profile of the newly emerged band is similar to the junction’s Tafel plot, in which the tunnel current increases steeply at the same voltage because of Fowler-Nordheim tunneling. The azo-band intensity change with elapsed time at +2.0 eV bias voltage is remarkable for the junction on the CaF_{2} roughened glass substrate. These results suggest that the PNBA reductive coupling reaction might correlate with surface plasmon polariton (SPP) excitations by the generated hot-electrons.

1. Introduction

Electron transfer between metals and adsorbates dominates surface fundamental processes, i.e., adsorption, desorption, and surface reactions [1]. Furthermore, that transfer is an important issue in recent molecule-based electronic devices [2]. Precise and tunable control in electronic states of the metal surface should be linked to development of novel molecular devices. Hot electrons, which have energies greater than the Fermi level of the metal, can access the unoccupied molecular orbital of adsorbates. Therefore, molecular states of the adsorbate can be controlled by the hot electrons [3]. The metal-insulator-metal (MIM) layout has been proposed for a hot-electron source; the top electrode might provide a useful template for promotion of a chemical reaction, e.g., for so-called "hot-electron chemistry" [4,5]. Although theoretical investigations into the dynamic behaviour of hot-electrons at the MIM electrode surface have been published [4,5], experimental studies of the hot-electron chemistry remain limited. Palmer and co-workers [6,7,8,9] investigated the tunnel characteristics of the Cu/SiO_{x}/Cu junctions and the decomposition of chlorinated hydrocarbons on the electrode surface. In addition, Otto and co-workers [10,11] reported precisely that the electrochemical reactions are promoted at the junction’s electrode surface. We have also reported the bias-voltage-induced decomposition of 2-methyl-1,4-naphthoquinone on the MIM tunnel junction [12]. Aside from those reports, Kirtley et al. [13] investigated Raman scattering from organic molecular layers at the oxide-metal interface of the MIM tunnel junctions to clarify surface enhanced Raman scattering (SERS) mechanisms: they concluded that the surface plasmon polariton (SPP) is an intermediate state in SERS.
This study is intended to demonstrate the MIM tunnel junction functions as a promoter of the surface reaction and to clarify the interaction process of the generated hot electrons with the surface molecule. We use SERS to investigate the hot-electron-induced surface reactions of p-nitrobenzoic acid (PNBA) adsorbed on Ag top electrodes in Ag/AlOₓ/Al tunnel junctions fabricated on bare and CaF₂-covered glass substrates. The results are summarized briefly in this paper.

2. Experimental

Details of the experimental equipment for the Ag/AlOₓ/Al tunnel junction fabrication and for the Raman measurements have been reported elsewhere [12,14]. A Pyrex glass plate (12×24×1 mm) and a 60-nm-thick CaF₂ pre-deposited Pyrex glass plate were used as substrates for the tunnel junctions. First, Al (99.999% purity) was deposited from a W basket on the substrates: the mass thicknesses were determined to be 30 nm using a quartz crystal microbalance. Then, the deposited Al film surfaces were oxidized in an oxygen atmosphere at ca. 770 K. Finally, 18-nm-thick Ag (99.999%) layers were evaporated from another W basket onto the resulting AlOₓ film surfaces. The positive and negative bias-voltage indicated in this paper refer respectively to electron tunnelling from Al to Ag and from Ag to Al. Subsequently, PNBA was cast onto the Ag surfaces by spin coating from a 0.01 M ethanol solution. A He-Ne laser (633 nm; 8 mW at the sample position) was used for Raman excitations. The Raman scattered light was dispersed using a polychrometer and detected using a liquid-N₂-cooled CCD detector (acquisition time was typically 60 s). All SERS measurements were carried out in air. Surface morphologies of the Ag electrodes formed on the substrates were imaged using an atomic force microprobe (AFM).

3. Results and discussion

![Figure 1](image1.png)

**Figure 1.** SERS spectral changes of PNBA on the Ag/AlOₓ/Al tunnel junction under (a) +3.0 V and (b) -3.0 V biased to the Ag electrode.

![Figure 2](image2.png)

**Figure 2.** Peak-shifts (top) and intensities (middle) of the adsorbed PNBA⁻ bands vs. bias voltages. Bottom: logI₀/ₐ₁-V curve recorded at 150 K.

Figure 1 shows the SERS spectral changes of adsorbed PNBA on the Ag/AlOₓ/Al fabricated on the bare-glass substrate as a function of positive (a) and negative (b) bias-voltages. The spectra recorded at ±0.0 eV are characterized by strong bands located at 1350, 1380 and 1580 cm⁻¹. In fact, PNBA is well known to adsorb dissociatively on the Ag surface to form PNBA⁻, which is a
"fingerprint" of the chemisorption onto the surface [15]. The three bands described above can be assigned respectively to COO\textsuperscript{-}, NO\textsubscript{2}, and phenyl groups of the adsorbed PNBA\textsuperscript{-}, thereby indicating that PNBA dissociatively adsorbs on the Ag electrode surface. It is noteworthy that the SERS bands increased in intensity with increasing positive bias-voltage, whereas the spectra remained nearly unchanged, even under negative-bias applications.

A new band emerges near 1450 cm\textsuperscript{-1} above +2.2 eV and increases with increasing positive bias-voltage. The PNBA adsorbed on the Ag substrate reacts in a reductive coupling reaction to generate azodibenzoate during SERS measurements [15,16]; the reaction product reveals a SERS band around 1450 cm\textsuperscript{-1}. Therefore, the azo-species is more or less generated on the junction's top electrode during SERS measurements. However, the SERS bands remained nearly unaltered after several spectral runs under negative bias-voltages (b), indicating that the light intensity at the sample surface is insufficient for generating the reductive coupling reaction. Figure 1 shows clearly that the hot electrons generated at the Ag electrode surface promote the reductive coupling reaction of the adsorbed PNBA\textsuperscript{-}.

The total processes induced under bias voltage to the tunnel junction are summarized as follows [5]: (1) hot-electron injection into the top electrode film; (2) hot-electron transport with attenuation across the film; (3) energy-dependent transmission or scattering of the hot electrons at the top electrode surface, e.g., the electrons emit into vacuum (so-called cold cathode), excite SPP at the metal-vacuum interface (then radiate), and undergo resonant scattering from an adsorbate (bond-selective excitation/reaction at the surface). Consequently, the Raman signal enhancements for the PNBA bands (Fig. 1) might stem either from increased enhancement of the local electric field because of the surface plasmon polariton (SPP) excitation [19] or from an increase in the amount of the adsorbed PNBA\textsuperscript{-} resulting from the enhanced local electric field. Furthermore, the enhanced local electric field might also engender the "hot-electron-induced" reductive coupling reaction of adsorbed PNBA\textsuperscript{-} to generate the azo-species. We have deconvoluted each band in Fig. 1 and evaluated the Raman intensity and frequency changes with positive bias voltage: the results of which are shown in Fig. 2. The Tafel plot (log\textit{I}_T-V) for the tunnel junction is also shown in the bottom. Diesing et al. [17] investigated electron tunnelling characteristics of the Al/AlO\textsubscript{x}/Ag junction based on the Tafel plots and showed that the Ag/AlO\textsubscript{x} band edge was sensitive to the barrier AlO\textsubscript{x} preparation condition. Figure 2 shows that tunnel current increases steeply above +2.2 eV because of Fowler-Nordheim tunnelling [18]. Therefore, the Ag/AlO\textsubscript{x} band edge for the junctions fabricated under our condition should be located at +2.2 eV above the Fermi level of Ag. It is remarkable that the intensity profile of the 1450 cm\textsuperscript{-1} band (red open circle) corresponds well to the junction’s Tafel plot. The results indicate clearly
that emergence of the new band correlates strongly with the hot electron generation under positive bias-voltage. Furthermore, the 1380 and 1580 cm$^{-1}$ bands show blue shifts and similar intensity profiles as for the 1450 cm$^{-1}$ band. In contrast, the nitro-band (1350 cm$^{-1}$; blue open diamond) shifts to a lower wavenumber and its intensity increases more gradually. The nitro-group directly contributes to the reductive coupling reaction. Therefore, the slow increase in intensity probably supports the conjecture that the hot-electron-induced coupling reaction takes place at the Ag surface.

To clarify the interaction process of the generated hot electrons with the adsorbed PNBA$^-$ in greater detail, the SERS spectra are recorded for the adsorbed PNBA$^-$ on the junction’s Ag top electrode surfaces fabricated on the bare and CaF$_2$-covered glass substrates: the results are shown in Fig. 3. Under the +2.0 eV bias-voltage application, the change in the azo-band (indicated by arrow) for the junction on the CaF$_2$ substrate (b) is remarkable in comparison to that on the bare-glass substrate. The AFM images for the junction’s Ag electrode surfaces (upper panel) reveal that the surface of (b) is rough on the sub-micrometer level. The SPP excitation is well known to depend strongly upon nanoscale surface roughness. Therefore, the results suggest that SPP excitations by the generated hot-electrons play an important role in the reductive coupling reaction of the adsorbed PNBA$^-$. 

4. Summary

We investigated the hot-electron-induced surface reaction of the PNBA$^-$ adsorbed on the Ag top electrode surface of the Ag/AlO$_x$/Al tunnel junctions fabricated on the bare and CaF$_2$-covered glass substrates using SERS. The azo-band that was generated through the reductive coupling reaction of the adsorbed PNBA$^-$ emerged under the positive-bias-voltage applications. Dependence of the azo-band’s intensity on the bias-voltage was similar to the junction’s Tafel plot, in which the tunnel current increased steeply at voltages greater than +2.2 eV because of Fowler-Nordheim tunnelling. Furthermore, hot-electron-induced reductive coupling reaction was enhanced for the junction fabricated on the CaF$_2$ roughened substrate. The PNBA$^-$ reductive coupling reaction might correlate with SPP excitations by the generated hot-electrons at the electrode surface.

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