Surface-Enhanced Resonance Raman Spectroscopy of Adsorbates on Semiconductor Electrode Surfaces: Tris(bipyridine) ruthenium(II) Adsorbed on Silver-Modified n-GaAs(100)

Richard P. Van Duyne* and Jeanne P. Haushalter

Department of Chemistry, Northwestern University, Evanston, Illinois 60201 (Received: March 31, 1983; In Final Form: June 6, 1983)

The first observations of surface-enhanced resonance Raman scattering (SERRS) from tris(bipyridine) ruthenium(II), Ru(bpy)₃²⁺, at monolayer (or less) coverage on n-GaAs(100) semiconductor (SC) electrodes modified by the electrodeposition of ca. 100 monolayers of Ag metal are reported. In addition to the SERRS studies, the photoelectrochemical and surface microstructural properties of Ag/GaAs/Ru(bpy)₃²⁺ electrodes were studied by cyclic voltammetry (CV) and scanning electron microscopy (SEM).

Introduction

Substantial progress has been made in recent years toward the development of semiconductor (SC)-based photoelectrochemical (PEC) devices for the sustained, efficient conversion of light to chemical or electrical energy. The basic chemistry and physics of such devices has been discussed in detail in many recent reviews. One of the most important findings in this research area is that the efficiency and longevity of PEC devices is strongly influenced by the surface properties (viz., surface structure, energetics, and redox kinetics) of the SC photoelectrode. These experimental studies have clearly shown that surface treatments such as chemical etching and chemical modification by chemisorption or by covalent derivatization have a profound effect. These studies have been interpreted as evidence for the existence of surface states that have electronic energy levels different from those allowed in the bulk SC. It is believed that surface states play an important role in SC photoelectrochemistry. Surface states arise from such structural features as lattice termination (viz., dangling bonds), lattice defects, or chemisorbed species.

It is clear that a more complete understanding of the chemical and physical nature of surface states on a molecular level would be beneficial so that PEC device performance could be altered on a more rational basis through the strategy of surface modification. A direct experimental route to achieving such a molecular description of SC surfaces requires the development of an in-situ, molecularly specific spectroscopic method. Unfortunately, the standard electron and particle surface spectroscopies (viz., Auger electron spectroscopy, X-ray and UV photoelectron spectroscopies, high-resolution electron energy loss spectroscopy, etc.) are less than ideal for this application due to either their lack of molecular specificity or their requirements for ultrahigh vacuum (UHV) operation. In spite of such limitations, these techniques have been applied to the ex-situ characterization of pretreated and/or chemically modified SC electrodes and have provided information about the atomic composition of and adsorbate coverage on these surfaces. Thus, for in-situ studies, it appears that surface Raman spectroscopy (SRS) is one of the few viable candidates for this molecular surface characterization problem. Other surface vibrational spectroscopies (viz., surface IR absorption/reflection spectroscopy, high-resolution electron energy loss spectroscopy, or inelastic electron tunneling spectroscopy) all suffer from incompatibility with solvent and electrolyte eother because of strong interference problems or operational constraints.

Surface Raman spectroscopy derives its monolayer sensitivity from one or both of two distinct enhancement mechanisms. The first is the well-known resonance Raman effect (RR), which involves localized electronic excitation of the adsorbate. The second, surface-enhanced Raman scattering (SERS), first discovered in this laboratory, leads to a ca. 10⁶-fold enhancement in the Raman scattering intensity for adsorbates on submicron roughened metal surfaces. The current status of SERS theory and exper-

References

iment is given in a number of recent reviews.26-29

SER or SERR spectra of more than 200 molecular species have now been reported. Thus it is apparent that these phenomena are quite molecule general. Furthermore, SERS and SERRS are also interface general since they have been observed at solid/liquid, solid/UHV, solid/gas, and solid/solid interfaces. However, SERS and SERRS are apparently not substrate general phenomena and, at present, have been convincingly shown to exist only on Ag, Au, Cu, Ag-Pd, Ag-Au, Li, and Na surfaces.

In this Letter we report the first successful application of a surface-enhanced resonance Raman (SERRS) process to the molecular characterization of a SC electrode surface. The lack of SERS and SERRS substrate generality has been circumvented in these experiments through the electrodeposition of a discontinuous overlayer of Ag onto Ru(bpy)$_3^{2+}$ treated n-GaAs electrodes. High signal-to-noise ratio (S/N) SERRS from Ru(bpy)$_3^{2+}$ chemisorbed at monolayer (or less) coverage have been observed. Ru(bpy)$_3^{2+}$ was chosen as the adsorbate because (1) Ru(bpy)$_3^{2+}$ has a well-characterized resonance Raman spectrum and well-defined redox properties, (2) Ru(bpy)$_3^{2+}$ has been used as a sensitizer for large bandgap SC electrodes, and (3) dramatic improvements have been reported in the performance of PEC devices based on n-GaAs photoanodes on which Ru$^{2+}$ is chemisorbed.13,20

Experimental Section

Materials. Single-crystal, Si-doped, n-type GaAs(100) wafers were obtained from Laser Diode Laboratories, Inc. The doping level was $0.05 \times 10^{18}-1.6 \times 10^{19}$ cm$^{-3}$. Spectroscopic grade solvents (viz., acetonitrile (ACN) and methanol from Burdick & Jackson), Ru(bpy)$_3Cl_2$-6H$_2$O (G. Frederick Smith), and AgNO$_3$ (Goldsmith) were used as received. Tetra-n-butylammonium perchlorate (TBAP), used as the supporting electrolyte for nonaqueous electrochemical experiments, was supplied by Southwest Analytic Chemicals, Inc. Before use, the TBAP was recrystallized twice from reagent grade ethyl acetate, dried in vacuo, and stored in a desiccator. Tetra-n-butylammonium chloride (TBACI) was obtained from Tridom/Fluka Chemical, Inc. and used as received.

SC Electrode Fabrication. n-GaAs electrodes were fabricated by cutting the wafers into ca. 0.5-cm$^2$ specimens and mounting them on 6-mm-diameter Pyrex tubing with solvent-resistant epoxy resin (Varian Associates Torr-Seal) or silicone rubber (General Electric RTV-112). These materials also served as the mask to define the ca. 0.4-cm$^2$ electroactive area. Ohmic contacts were made to n-GaAs by mechanically abrading the back of the crystal, wetting it with Ga-In alloy, and attaching a flattened or coiled Cu wire lead to the alloy coating with Ag epoxy (EPO-TEK 417). The Cu wire lead was passed out through the tip of the Pyrex tubing electrode holder and secured with Torr-Seal epoxy.

Cyclic Voltammetry. All cyclic voltammetry (CV) experiments were performed in "sandwich-type" Raman spectroelectrochemical cells of the kind previously described in the literature.25 The potentiostat and triangular wave generator were of conventional operational amplifier design and are described in detail elsewhere.22 Cyclic voltammograms were recorded on a Hewlett-Packard 7015B X-Y recorder. Illumination of the GaAs SC electrodes for photoelectrochemical experiments was performed by a 2-mW He-Ne laser (Coherent Radiation Model 80). A 40-mm f plano-convex lens was placed between the laser and the photoelectrochemical cell. By adjusting the distance between the electrode surface and the laser focal spot the entire electroactive area of the SC electrode was illuminated.

Raman Spectroscopy. All of the Raman spectra reported here were acquired by using ca. 100 mW of laser power from the 457.9-nm line of a Coherent Radiation Laboratories Model CR-3 argon ion laser. The double monochromator, photon-counting detection electronics, photomultiplier tube, and computerized data acquisition system have all been described.33 The monochromator bandpass for all experiments was 4 cm$^{-1}$. All Raman spectra reported here are for ex-situ SC electrodes (i.e., GaAs/air interface) examined in the backscattering geometry. In-situ experiments will be reported in a future publication.41

Scanning Electron Microscopy. SEM's were taken on two different microscopes. Low-resolution experiments (250 Å) were conducted on a JOEL Model JSM-50A and higher-resolution studies (30-40 Å) were performed on an AMRAY, INC. Model 1400T equipped with a particle size measurement system. Specimens were mounted with conducting Ag paint but were not gold coated since surface charging was not a problem.

Results and Discussion

The method of preparation for the SERRS-active n-GaAs SC electrodes used in this study involved three steps: (1) an etch in a stirred solution of H$_2$SO$_4$ (30%)/H$_2$O$_2$ (1:1

Figure 1. Cyclic voltammmograms in 1.0 mM Ru(bpy)$_3^{2+}$/0.1 M TBAP/acetonitrile. Scan rate was 0.1 V/s: (A) n-GaAs in the dark; (B) n-GaAs with 632.8-nm illumination; (C) Pt.


**Figure 2.** Cyclic voltammograms in 10 mM AgNO₃/0.1 M TBAP/acetonitrile. Scan rate was 0.1 V/s: (A) n-GaAs in the dark; the dashed line indicates zero current; (B) Pt.

by volume) for 30 s to prepare a smooth, shiny surface; (2) exposure of the etched electrode to a 1.0 mM solution of the RR probe molecule, Ru(bpy)₃²⁺, in 0.1 M TBAP/ACN followed by the execution of a single, dark cyclic voltammetric scan identical with the one shown in Figure 1A, removal of the electrode from the Ru(bpy)₃²⁺/TBAP/ACN solution, and thorough rinsing with ACN to remove non-adsorbed Ru(bpy)₃²⁺; and finally (3) immersion of the rinsed electrode in a 10 mM AgNO₃/0.1 M TBAP/ACN solution and electrodeposition of a discontinuous Ag overlayer. The SC electrode was not illuminated during the Ag electrodeposition step. Following this treatment, electrodes were rinsed with copious amounts of both methanol and ACN to remove any material not strongly adsorbed to the electrode surface. Raman spectra were then recorded as described above.

The cyclic voltammetric behavior of n-GaAs electrodes prepared as described above are shown in Figures 1 and 2. In some cases the corresponding experiment on a platinum metal electrode is shown for comparison. Figure 1A and C, shows the dark cyclic voltammetry of an etched n-GaAs SC electrode and a Pt metal electrode, respectively, in a 1.0 mM Ru(bpy)₃²⁺/0.1 M TBAP/ACN solution. The Ru(bpy)₃²⁺ reduction waves occur at more negative potentials on dark n-GaAs than the corresponding wave on Pt. This electrode is photoelectrochemically active as demonstrated by the fact that under illumination (see Figure 1B) the redox processes for Ru(bpy)₃⁵⁺, Ru-(bpy)₃⁶⁺, and Ru(bpy)₃⁸⁺ observed on the reverse sweep occur at more negative potentials than they do on either dark n-GaAs or Pt. These results are in good agreement with those of Bard¹⁴ considering the sensitivity of SC electrode CV to details of the surface preparation.

Figure 1B also shows a photoassisted oxidation at +0.05 V vs. SCE. This oxidation is clearly associated with the presence of Cl⁻ from Ru(bpy)₃Cl₂·6H₂O. When the perchlorate salt of Ru(bpy)₃²⁺ is used, this wave is absent. Furthermore, this wave is observed in 0.01 M TBACl/0.1 M TBAP/ACN solution. Photooxidation of Cl⁻ to Cl₂ is unlikely because this would require a photovoltage approaching the theoretical maximum. Therefore, a more probable assignment is a photoassisted GaAs surface ox-

**Figure 3.** Scanning electron micrographs of n-GaAs electrodes: (A) etched to a shiny finish; (B) etched to shiny with Ag overlayer; (C) same as B but higher magnification. The checkered bar indicates a particle size measurement of 0.23 μm.
oxidation, possibly photoanodic dissolution of the GaAs lattice, involving the participation of Cl-.

Figure 2 shows cyclic voltammograms for Pt and n-GaAs in 10 mM AgNO3/0.01 M TBAP/ACN solution. By scanning a single cyclic voltammogram (as depicted in Figure 2A), a discontinuous layer of Ag was deposited. The amount of Ag deposited can be determined from the area under the cyclic voltammetric wave. The result for the voltammogram in Figure 2A shows that 30 mC/cm² of charge was passed in depositing the Ag overlayer which is equivalent to ca. 120 monolayers. However, high S/N SERRS spectra are obtainable with Ag coverages of 50, 20, or even 10 monolayers and in fact the S/N is improved at the lower coverages. In the dark, essentially no Ag is stripped on the reverse scan. However, some stripping of Ag will occur if n-GaAs is illuminated. Ag deposits at much more negative potentials on n-GaAs than on Pt or p-GaAs.

Although the purpose of depositing Ag on n-GaAs in this experiment was strictly in order to obtain SERRS spectra of adsorbed species on the electrodes, it should be noted that the n-GaAs electrode retains its photoelectrochemical properties with the Ag overlayer as will be reported in detail in a future paper. Furthermore, metal overlayers on SC electrodes have been used to enhance the efficiency and stability of SC electrodes in PEC devices.

Figure 3 shows scanning electron micrographs of electrodes treated as described above. Figure 3A shows an electrode which was subjected to steps 1 and 2 only (i.e., no Ag was deposited). Figure 3, B and C, shows an electrode which underwent all 3 steps of preparation. It can be seen that Ag deposit in clusters of microparticles which are ca. 0.25 μm in diameter on the average. The checkered line on Figure 3C corresponds to a particle measurement of 0.23 μm. This dimension is smaller than the wavelength of light used in the Raman experiments as required by the electromagnetic field enhancement theories of SERS.

Figure 4 shows three Raman spectra taken on three different electrode surfaces. The excitation wavelength was 457.9 nm which corresponds very closely to the low-energy absorption maximum of Ru(bpy)²⁺. Spectrum 4a corresponds to an electrode treated as described in steps 1 and 2. This spectrum shows only the LO and TO phonon bands of GaAs. Spectrum 4b is for an electrode subjected to all three treatment steps (i.e., a Ag overlayer was deposited). Here the characteristic vibrational bands of Ru(bpy)²⁺ are very apparent. The seven modes between 1000 and 1700 cm⁻¹ are due to the bipyridine ligands. The other major features in spectrum 4b are also present in spectrum 4c which is for an electrode which was not exposed to Ru(bpy)²⁺ but otherwise treated identically to the electrode represented by spectrum 4b. The broad features between 1100 and 1700 cm⁻¹ are characteristic of amorphous carbon islands on the surface.

Along with carbon contamination, Ag/GaAs surfaces have oxide contamination which can arise from various sources. Oxides of Ga and As are formed on the GaAs surface upon etching. There could be formation of a Ag oxide when Ag is deposited on this GaAs oxide layer. In addition, partial oxidation of the Ag island film after deposition is almost a certainty. The low-frequency region of spectrum 4c shows a number of broad features, the most prominent being centered at about 800 cm⁻¹. These features are most probably due to amorphous oxide phases of Ga, As, and Ag on the Ag/GaAs surface. This tentative assignment is based on the following evidence: (1) the SER spectrum of a "cold Ag film", which has been exposed to O₂ shows bands at 1045, 808, 832, and 687 cm⁻¹; (2) oxide species of both As and Ga have Raman modes in the vicinity of 800 cm⁻¹; and (3) the spectral pattern observed in spectrum 4c appears to be characteristic of GaAs (i.e., it is not observed when Ag island films are deposited on other substrates). Since spectrum 4c shows no distinct sharp modes, it is reasonable to assume that amorphous phases and/or mixtures of oxides are present on the surface. One can conclude, therefore, that SERS/SERRS has the potential to be an in-situ monitor of carbon as well as oxide contamination of the Ag/GaAs surface.

There are observable vibrational spectroscopic differences between Ru(bpy)²⁺ adsorbed on Ag/GaAs and free in solution. The solution spectrum of Ru(bpy)²⁺ excited by 457.9-nm CW Ar⁺ laser light has been previously reported. Comparing surface 4B with the solution spectrum in ref 30, we find (1) no frequency shifts greater than ca. 1 cm⁻¹; (2) an 1.5 × broadening of all the observed lines, and (3) the development of a shoulder or asymmetry in the line shape on the low-frequency side of some lines (see, for example, the low-frequency asymmetry in the 1497-cm⁻¹ band in Figure 4B). From the fact that the

---

spectroscopic differences between adsorbed and free Ru(bpy)$_3^{2+}$ are quite small, we infer that no ligand dissociation has taken place during the chemisorption process. This inference is based on our studies of SERS/SERRS and RRS of Ru(bpy)$_3$Cl$_2$ which shows easily discernible spectral changes relative to Ru(bpy)$_3^{2+}$. Given that Ru(bpy)$_3^{2+}$ is not dissociatively chemisorbed on Ag/GaAs, it is possible to understand why the observed spectral differences between the adsorbed and free molecules are small. Ru(bpy)$_3^{2+}$ is a very large, high-symmetry molecule (viz., $D_3h$ point group) possessing many ligand-centered, strongly coupled normal modes capable of distributing an adsorption induced structure change so that the resulting frequency shifts are very small.

The surface coverage of Ru(bpy)$_3^{2+}$ on GaAs in these experiments is believed to be less than 1 monolayer based on the following indirect evidence: (1) in the experiments reported here, both resonance and surface enhancement were required in order to observe high S/N spectra from adsorbed Ru(bpy)$_3^{2+}$; (2) submonolayers of strongly resonant Raman active molecules on surfaces yield high S/N spectra even without surface enhancement; and (3) in experiments to be reported separately, we have observed high S/N SERRS from Ru(bpy)$_3^{2+}$ chemisorbed on Ag/p-GaAs surfaces where the maximum possible surface coverage of the RR probe molecule was restricted to one monolayer by exposing a set of p-GaAs wafers of known surface area to an ACN solution volume containing the number of Ru(bpy)$_3^{2+}$ molecules equivalent to one monolayer.

It is not certain that the Ru(bpy)$_3^{2+}$ detected by SERRS is, in fact, chemisorbed on the GaAs surface after the electrochemical deposition of Ag. However, since Ru(bpy)$_3^{2+}$ SERR spectra of comparable intensity are obtained independent of whether Ag is vacuum deposited, photochemically deposited, or photoelectrochemically deposited on n- or p-GaAs (which have very different Ag deposition potentials), it is very probable that Ru(bpy)$_3^{2+}$ remains adsorbed to GaAs.

Conclusions

In this Letter we have demonstrated the first application of surface-enhanced Raman spectroscopy to the molecular surface characterization of a semiconductor photoelectrode. We have observed SERR spectra for a monolayer or less of an intentionally adsorbed sensitizer, Ru(bpy)$_3^{2+}$, as well as for surface carbon contamination. These results have been achieved by a surface modification process that induces surface enhancement on GaAs while minimally perturbing its photoelectrochemical properties. We believe that this strategy opens up a new methodology for the in-situ molecular surface characterization of SC photoelectrodes.

Acknowledgment. The authors acknowledge the generous support of this research by the Office of Naval Research (Contract No. N00014-79-C-0369) and Dr. Maria Janik-Czachor for the SEM photograph in Figure 3A.

Surface-Enhanced Raman Spectroscopy of Platinum.\(^1\) 2. Enhanced Light Scattering of Chlorine Adsorbed on Platinum

B. H. Loo

Department of Chemistry, The University of Alabama in Huntsville, Huntsville, Alabama 35899 (Received: April 4, 1983)

Surface-enhanced Raman scattering has been observed from electrogenerated chlorine adsorbed on a platinum electrode with 488-, 496.5-, and 514.5-nm Ar$^+$ and 647.1- and 676.4-nm Kr$^+$ laser excitation wavelengths. Two vibrational features at 509 and 541 cm$^{-1}$ with an approximate intensity ratio of 1:2 are assigned to the surface vibrations of bridged and linear chlorine on platinum, respectively. This is the first report of a surface vibrational spectrum of molecular chlorine adsorbed on a metal surface.

Introduction

The group 1B metals (Cu, Ag, and Au) were first shown to exhibit unambiguous surface-enhanced Raman scattering (SERS), and several theoretical models (electrodynamic models) based on the optical properties of these metals have been proposed.\(^2\) These metals have the common optical property that their plasmons are weakly damped in the visible region where laser excitation occurs. The second group of theories (electronic models) involves the electronic interaction between the metal and the adsorbate.\(^3\) This group of theories requires a favorable configuration of electronic levels in the molecule; however, there is no general requirement on the optical properties of the substrate. In principle, SERS may occur on any metal if the bonding between the metal substrate and the adsorbate were compatible.

Platinum is one of the best catalysts known, thus extending the analytical capability of the SERS technique to the study of adsorption on Pt is of great interest in both

---