Surface-Enhanced Resonance Raman Spectroscopy of Adsorbates on Semiconductor Electrode Surfaces. 1 2 In Situ Studies of Transition Metal (Fe and Ru) Complexes on Ag/GaAs and Ag/Si

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Various aspects of surface-enhanced resonance Raman spectroscopy (SERRS) of adsorbates (viz., Ru(bpy)2+, Fe(bpy)2+, Fe(phen)3+) on semiconductor (SC) electrodes with Ag overlayers are examined. In situ SERRS spectra are reported for a nonaqueous electrode system, and SERRS signals are monitored with time as Ag is deposited on SC electrode surfaces both electrochemically and photochemically. Other topics to be covered include the resonance enhancement contribution to SERRS, optimum Ag coverages, and enhancement factors. The photoelectrochemistry of Ag/GaAs electrodes is discussed as well as the implications of the SERRS overlay technique for photoelectrochemical research.

Introduction

In a recent letter, 1 we demonstrated that adsorbed species on semiconductor (SC) electrode surfaces can be detected by surface-enhanced resonance Raman scattering (SERRS) by layering the SC surface and adsorbing with a discontiguous film of Ag. The SERRS effect was thereby exploited for the study of an adsorbate, tris(bipyridine)ruthenium(II), on the non-SERS-active substrate n-GaAs(100). This work is significant from two points of view—that of both the photoelectrochemical and surface-enhanced Raman scattering (SERS)/SERRS research communities.

Detection and identification of adsorbates on SC electrode surfaces are of paramount importance to photoelectrochemical research because adsorbed species can give rise to surface states which in turn affect interface energetics. 2-10 Surface states can lead to a number of deleterious effects in photoelectrochemical cells (PECs) based on the SC–liquid junction, including Fermi level pinning 11-13 and electron–hole (e–h+) pair recombination. 14 Consequently, a molecularly specific probe technique with monolayer sensitivity (such as SERS/SERRS) would be of great value to the study of SC electrode surfaces. The work reported in ref 1 demonstrated the ex situ spectroscopy of monolayers on SC electrode surfaces and suggested that reactions may be studied in situ with monolayer sensitivity on non-SERS electrode surfaces.

The work reported here is also of general interest to SERS/SERRS research. The study of systems involving non-SERS substrates and SERS metal island films will contribute to the large body of experimental information which will be required to finally determine which mechanisms lead to the millionfold enhancement of Raman scattering observed in SERS. 15-21 Non-SERS substrates can be divided into three major categories defined by their dielectric properties (i.e., transition metals, semiconductors, and insulators). The work begun in the experiments to be reported here will contribute to studies of the semiconductor category. Among the topics covered here are: (1) in situ studies of Ag/GaAs/adsorbate electrode surfaces, (2) the generality of the SERRS phenomena observed by the overlay technique, (3) photochemical (electroless) deposition of Ag on p-GaAs and p-Si, (4) some quantitative aspects of the SERRS experiments, (5) the photoelectrochemistry of Ag/GaAs electrodes, and (6) the location of the molecules giving rise to the surface-enhanced Raman scattering with respect to the Ag surface microstructures.

Experimental Section

Materials. Single-crystal, n- and p-type (Si and Zn doped, respectively) GaAs(100) wafers were obtained from Laser Diode Laboratories, Inc. Boron-doped p-Si(100) was obtained from Microtec. Dopant densities were typically 1011 cm–2. Spectroscopic grade solvents (viz., acetonitrile (ACN) and methanol from Burdick & Jackson), Ru(bpy)3Cl2–6H2O (G. Frederick Smith), and AgNO3 (Goldsmith) were used as received. Tetra-n-butylammonium perchlorate (TBAP), used as the supporting electrolyte for nonaqueous electrochemical experiments, was supplied by Southwest Analytical Chemicals, Inc. Before use, the TBAP was recrystallized twice from reagent grade ethyl acetate, dried in vacuo, and stored in a desiccator. Aqueous solutions of Fe(bpy)2+, Fe(phen)3+, and Fe(bpy)3+, were prepared by mixing stoichiometric amounts of FeSO4·7H2O (Mallinckrodt) and ligand (viz., 2,2'-bipyridine and 1,10-phenanthroline (Aldrich)) in a ca. 25-mL volume of distilled H2O. Insoluble material was drawn into solution as the complexation reaction progressed. Ruthenium complexes were used as received from the following suppliers: Ru(NH3)6Cl3 from Strem Chemicals, Inc., Ru(bpy)3Cl2 from Spex

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(22) R. P. Van Duyne and K. T. Carron, unpublished work.
Industries, Inc., and K$_4$Ru(CN)$_6$·3H$_2$O from Alfa Products.

**SC Electrode Fabrication.** GaAs and Si 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 top of the Pyrex tubing electrode holder and secured with Torr-Seal epoxy.

**Cyclic Voltammetry.** Cyclic voltammetry (CV) experiments were performed in "sandwich-type" Raman spectroelectrochemical cells of the kind previously described in the literature. The potentiostat and triangular wave generator were of conventional operational amplifier design and are described in detail elsewhere. Cyclic voltammograms were recorded on a Hewlett-Packard 7015B X–Y recorder. Illumination of the Ag/GaAs electrodes for photoelectrochemical experiments was provided by a 2-mW He–Ne laser (Coherent Radiation Model 80). A 40-mm focal length 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, we could illuminate the entire electroactive area of the SC electrode.

**Raman Spectroscopy.** All of the Raman spectra reported here were acquired by using ca. 100 mW of laser power from the 457.9- or 514.5-nm line of a Coherent Radiation Laboratories Model CR-3 argon ion laser. The double monochromator, photon-counting detection electronics, photomultiplier tube, and computer/data acquisition system have all been described. The monochromator band-pass for all experiments was 4 cm$^{-1}$. Backscattering geometry was used in both in situ and ex situ experiments.

**Scanning Electron Microscopy (SEM).** Scanning electron micrographs were taken with a JOEL Model JSM-50A SEM. Specimens were mounted with conducting Ag paint but were not gold plated since surface charging was not a problem.

**Results and Discussion**

**In Situ Experiments.** The real power of the SERS technique is fully appreciated when a research problem requires in situ studies of an electrode surface. The electrochemical cell environment is not compatible with such vibrational surface spectroscopies as high-resolution electron energy loss spectroscopy (HREELS) and inelastic electron tunneling spectroscopy (IETS). Surface infrared spectroscopy still suffers from solvent interference problems as in aqueous solution and is, therefore, limited to studies in thin-layer electrochemical cells. The SERS technique is really the only option available for in situ studies of a SC electrode surface in aqueous electrolyte. Prior to this work, and another study from our group, SERS phenomena had never been observed in nonaqueous solution. However, Figure 1 shows that the SERS technique is quite applicable to in situ studies in acetonitrile.

Figure 1A shows a SERS spectrum of a Fe(bpy)$_3$$^{2+}$-treated n-GaAs electrode in 10 mM AgNO$_3$/0.1 M TBAP/ACN at −0.5 V vs. Ag/Ag$^+$ (0.01 M) electrode. In this case a Ag overlay was deposited by scanning a single sweep cyclic voltammogram (CV) between −0.5 and 2.0 V vs. Ag/Ag$^+$ (0.01 M). Figure 1B shows the spectrum of same electrode before the Ag was deposited.

![Figure 1](image1.png)

**Figure 1.** (A) SERRS spectrum of Fe(bpy)$_3$$^{2+}$ adsorbed on n-GaAs in 10 mM Ag$^+$/0.1 M TBAP/ACN after CV at −0.5 V vs. Ag/Ag$^+$ (0.01 M). (B) Raman spectrum taken at n-GaAs surface in 10 mM Ag$^+$/0.1 M TBAP/ACN before CV at −0.5 V vs. Ag/Ag$^+$ (0.01 M). Acetonitrile bands are labeled S. $\lambda_{514}$ = 457.9 nm, laser power = 100 mW, monochromator band-pass = 4 cm$^{-1}$, and scan rate = 1 cm$^{-1}$/s.

Figure 2 shows a plot of SERRS signal intensity at 1496 cm$^{-1}$ as a function of time as Ag is deposited by scanning a single sweep CV (inset): A, −2.0 V; B, −0.5 V (end of cyclic scan). Ru(bpy)$_3$ adsorbed on n-GaAs. $\lambda_{514}$ = 457.9 nm, laser power = 100 mW, and monochromator band-pass = 4 cm$^{-1}$.

![Figure 2](image2.png)

**Figure 2.** SERRS intensity at 1496 cm$^{-1}$ as a function of time as Ag is deposited by scanning a single sweep CV (inset): A, −2.0 V; B, −0.5 V (end of cyclic scan). Ru(bpy)$_3$ adsorbed on n-GaAs. $\lambda_{514}$ = 457.9 nm, laser power = 100 mW, and monochromator band-pass = 4 cm$^{-1}$.

Only acetonitrile bands (labeled S) are observed in Figure 1B while in Figure 1A, bands due to Fe(bpy)$_3$$^{2+}$ adsorbed to the GaAs surface are evident. The broad feature centered at ca. 1500 cm$^{-1}$ in Figure 1B is due to carbon contamination of the surface.

Figure 2 shows a plot of SERRS signal intensity at 1496 cm$^{-1}$ as a function of time as a CV was scanned to deposit Ag on a Ru(bpy)$_3$$^{2+}$-treated n-GaAs electrode. The signal was monitored for an additional 100 s after the Ag deposition was complete. At the end of the cyclic scan, only ca. 50% of the signal intensity had developed. As soon as the maximum signal was reached, it immediately began to decay. The behavior of the signal at times less than 100 s (during scanning of CV) is fairly reproducible and probably due to potential dependence of the signal as well as a Ag particle size effect. Because of the complexity of the phe-
Figure 3. (A) SERRS spectrum of Fe(phen)$_2^{2+}$-treated n-GaAs/Ag electrode ($\lambda_{exc} = 457.9$ nm). (B) Same as (A) except $\lambda_{exc} = 514.5$ nm. (C) SERRS spectrum of n-GaAs/Ag electrode (no adsorbate, $\lambda_{exc} = 514.5$ nm, laser power = 100 mW, monochromator band-pass = 4 cm$^{-1}$, and scan rate = 1 cm$^{-1}$/s). These are ex situ spectra.

Some phenomena associated with SERRS, it is difficult to interpret these data. Performing this experiment in a multichannel spectral data acquisition mode should help to clear up the questions about the time evolution of the SERRS signal with time.

Generality of the Ag Overlayer Technique. Adsorbed Fe-(bpy)$_2^{2+}$ and Ru(bpy)$_2^{2+}$ can be detected on n-GaAs by SERRS using the Ag overlayer technique as shown in Figures 1 and 2, respectively. Other complexes of Fe and Ru have been detected as adsorbates on GaAs by this method as well and experiments with this series of compounds served to illustrate the importance of resonance enhancement to the detection of adsorbed species on Ag/GaAs.

Figure 3 shows ex situ SERRS spectra for a Fe(phen)$_2^{2+}$-treated n-GaAs electrode with an electrochemically deposited Ag overlayer taken at two excitation wavelengths (457.9 nm for 3A and 514.5 nm for 3B). Fe(phen)$_2^{2+}$ has an absorption maximum at ca. 510 nm. Obviously the resonance enhancement contribution to the signal was crucial for detection of Fe(phen)$_2^{2+}$ in this case. Figure 3C shows the SERRS spectrum of a Ag/GaAs electrode, which was not treated with an adsorbate, for comparison.

SERRS and SERS spectra have been obtained for Ru(bpy)$_3^{2+}$Cl$_2$, Ru(CN)$_6^{3-}$, and Ru(NH$_3$)$_6^{3+}$ adsorbed on n-GaAs by this technique, but for the latter two species, which are not resonance enhanced in the visible region, the spectra were very weak.

A number of experiments have been conducted with other possible adsorbate/SC electrode systems for which no SERRS spectra were obtained—notably ferrocene/Si, I$_2$/MoS$_2$, and I$_3$/Si. Negative results in these cases may be attributed to poor adsorption or lack of resonance enhancement or both. It may also be the case that some adsorbate systems are not compatible with electrochemical Ag deposition. However, it is clear from other recent work$^{29,32}$ that Ag island film overlayers can impart SERRS detectability to adsorbates on a wide range of non-SERS substrates and that the overlayer technique is of general applicability.

Photochemical (Electroless) Deposition of Ag on p-GaAs and p-Si. On p-GaAs, Ag is deposited photochemically according to the reaction

$$\text{p-GaAs/e}^- + \text{Ag}^+ \rightarrow \text{p-GaAs/Ag}^0$$

where p-GaAs/e$^-$ represents p-GaAs with photogenerated surface electrons. Upon illumination, e$^-$/h$^+$ pairs are created near the surface of the p-GaAs substrate. Because of the band bending near the surface produced when the SC–liquid junction is formed, holes (h$^+$) are drawn into the bulk while electrons (e$^-$) migrate to the surface. Surface electrons are then available to reduce Ag$^+$ cations which diffuse to the surface. As Ag deposits in microcrystallites, a random array of Schottky junctions are formed, changing the surface energetics. The deposition reaction appears to be self-limiting either due to changes in surface energetics or decreased absorption of light by p-GaAs through the Ag overlayer.

Figure 4 shows a spectrum of a Ru(bpy)$_3^{2+}$-treated p-GaAs electrode (at open circuit potential) in 10 mM AgN$O_3$/0.1 M TBAP/ACN.

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is essentially stabilized when SERRS was focused on a sharp white line where the laser was focused. Scanning electron micrographs show that Ag deposits in individual microcrystallites with an average diameter of less than 200 nm.

When evolution of the SERRS signal at 1496 cm\(^{-1}\) is followed as a function of time, the curve in Figure 5A is obtained. As time \(= 0\) s, the p-GaAs surface is translated so that the laser is focused on a new spot. The signal increases monotonically for 70 s and then begins to fall off slowly. The signal level eventually stabilizes as is evidenced by the fact that spectra requiring 30-min scan times show proper relative intensities for the various bands of Ru(bpy)\(^{3+}\). Figure 5B is a background vs. time scan which is essentially flat as compared to the curve in Figure 5A. Figure 5C illustrates the effect of depositing too much Ag. Excess Ag was deposited by scanning a single sweep CV. The cyclic scan was complete at time \(= 100\) s. As the excess Ag is deposited (on top of the photochemically deposited line of Ag), the signal drops precipitously. On the second half of the cyclic scan, Ag is partially stripped causing the signal to recover somewhat (between time \(= 70\) and 100 s).

When electrodes were removed from solution after photochemical Ag deposition, it was not possible to obtain high-intensity SERRS spectra ex situ. The SERRS signals decayed very quickly when the intense laser radiation was focused on the photochemically deposited Ag in Air. The deterioration of the signal was too fast to capture as a signal transient.

Figure 6A shows a SERRS spectrum of a Ru(bpy)\(^{3+}\)-treated p-Si electrode in 10 mM AgNO\(_3\)/0.1 M TBAP/ACN solution. Ag is deposited on this substrate in a manner analogous to the reaction on p-GaAs. Figure 6B is a spectrum of an untreated p-Si electrode in the same medium as Figure 6A which shows only acetonitrile bands.

**Quantitative Aspects.** At this point, we would like to examine some quantitative aspects of these experiments. Among the questions which need to be addressed are (1) what is the optimum amount of Ag? (2) what is the approximate coverage of Ru(bpy)\(^{3+}\) on GaAs? and (3) what is the SERRS enhancement factor for these systems?

The optimum amount of Ag is related to the size and distribution of particles on the GaAs substrate and probably varies with the mode of deposition. Figure 5C clearly shows that too much Ag has a detrimental effect on the SERRS signal as would be expected. Figure 7 shows SERRS spectra of Ru(bpy)\(^{3+}\)-treated n-GaAs electrodes with different amounts of Ag deposited photochemically at \(-1.5\) V vs. Ag/Ag\(^+\) (0.01 M) reference electrode. Figure 7A is an electrode with ca. 10 monolayers of Ag while Figure 7B is for an electrode with ca. 40 monolayers. The additional Ag serves only to increase the background of the spectrum while the Ru(bpy)\(^{3+}\) bands remain at the same intensity. Therefore, the optimum amount of Ag is at or below the 10 monolayer level. It is possible to obtain SERRS spectra for adsorbates on GaAs with as little as 1–2 monolayers of Ag deposited in this manner. It should be noted that the spectra presented in Figure 7 are fairly weak, presumably because of low Ru(bpy)\(^{3+}\) coverage on the GaAs surface. It may be that smaller amounts of Ag are optimum for low Ru(bpy)\(^{3+}\) coverages, particularly if Ag initially deposits at sites where Ru(bpy)\(^{3+}\) is adsorbed.

Figure 8 shows the SERRS signal vs. time curve for a n-GaAs electrode obtained by monitoring the 1496-cm\(^{-1}\) band while a second Ag overlayer is deposited by scanning a single sweep CV (0.0–2.0 V). Prior to the second Ag deposition the SERRS signal
at 1496 cm\(^{-1}\) decayed from 15,000 to ca. 4000 counts. Clearly, the second deposition causes the signal to recover. The signal develops in much the same way as in the experiment depicted in Figure 2. Examination of the Ag/n-GaAs electrode by scanning electrode microscopy shows that Ag deposits in large clusters rather than in an even overlayer, leaving bare spots on the surface as seen in Figure 9. The scanning electron micrograph and the accompanying Ag X-ray image were taken soon after the curve in Figure 8 was obtained. It is clear from this experiment that it is not the amount but the morphology of the Ag which is important for the SERRS signal. Apparently there is an optimum morphology (roughness) which develops soon after the Ag is deposited but which has a fleeting existence. The second deposition serves to renew this condition temporarily, causing the Raman scattering from adsorbates on GaAs near the Ag clusters to be enhanced more efficiently.

In order to determine a SERRS enhancement factor for these systems, it is necessary to measure the coverage of adsorbate (Ru(bpy))\(^{2+}\) on the GaAs substrate. This coverage can vary depending upon how the GaAs etches, which in turn is affected by the type and amount of contamination or surface films present before etching. Experiments in which the amount of solution Ru(bpy))\(^{2+}\) taken up by GaAs powder was measured indicated that Ru(bpy))\(^{2+}\) adsorbs at no more than monolayer coverage. These results are corroborated by the spectrum in Figure 10 which is of a p-GaAs wafer in 10 mM AgNO\(_3\)/0.1 M TBAP/ACN. Ag was deposited photochemically on this wafer which was exposed to a restricted amount of Ru(bpy))\(^{2+}\) sufficient only to allow one monolayer coverage. The Ru(bpy))\(^{2+}\) bands in this spectrum are comparable in intensity to those of the solvent (acetonitrile). Experiments in which a series of evaporated films of Ru(bpy))\(^{2+}\) on GaAs were prepared suggested that the detection limit for Ru(bpy))\(^{2+}\) on GaAs by resonance Raman scattering alone (no SERS) is ca. 1–2 monolayers. In ref 1 we showed that no Ru(bpy))\(^{2+}\) was detectable by RRS alone after rinsing the GaAs surface thoroughly. Thus, it can be concluded that, in our experiments, Ru(bpy))\(^{2+}\) coverage is typically submonolayer. Experiments with the evaporated films also suggest an incremental surface enhancement factor of 10\(^2\)–10\(^3\). This value agrees with that obtained by other works\(^{22,31}\) for resonance-enhanced species on Ag island films.

**Photoelectrochemistry of Ag/GaAs.** In order to exploit the SERRS technique to observe photoelectrochemical reactions in situ with monolayer sensitivity, the Ag modified SC electrode must retain its photoelectrochemical properties. Deposition of metal overlayers has been an effective tactic used by several workers to protect SC electrode surfaces and to enhance their perform-

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The effect of a Ag overlayer on the photoelectrochemical behavior of n-GaAs is appreciable as depicted in Figure 11. The Ag overlayer causes an increase in the capacitive background current in the cyclic voltammograms. Also, when the illumination is chopped, only the anodic current is modulated on n-GaAs, but on Ag/n-GaAs both the anodic and cathodic currents are modulated. However, it is clear that the Ag/n-GaAs electrode is still photoelectrochemically active and it is conceivable that photoelectrochemistry could be monitored with SERRS dynamically at an Ag/n-GaAs electrode surface.

Figure 12 shows the result of a SERRS experiment involving a Ag/p-GaAs electrode (the p-GaAs retained its photoelectrochemical properties as evidenced by its photocurrent) in situ in M Ru(bpy)$_2^{2+}$/0.1 M TBAP/ACN. The spectra obtained are as follows: Figure 12A is a SERRS spectrum of Ru(bpy)$_2^{2+}$ on Ag/p-GaAs at $-1.0$ V vs. Ag/Ag$^+$ (0.01 M); Figure 12B is the same as 12A except the potential was modulated between $-1.0$ and $-2.0$ V by using a period of 100 ms; and for Figure 12C the potential was static at $-0.5$ V, and this spectrum was taken after the modulation experiment. It is clear that at very negative potentials a change in the intensity pattern of the spectrum occurs and red-shifted shoulders have grown on in the 1496- and 1036-cm$^{-1}$ bands. Also, the 1281-cm$^{-1}$ band (assigned to a C=C stretch with C-H wag) is increased in intensity and considerably broadened. The 1496-cm$^{-1}$ band is assigned to a mode involving both C=N and C=C stretching plus C-H wag while the 1036-cm$^{-1}$ band is attributed to the C=C ring-ring stretch and C-H wag. The spectrum in Figure 12B does not resemble spectra of the MLCT species of Ru(bpy)$_2^{2+}$ which is believed to contain a (bpy$^-$) moiety. This suggests that the differences observed in our experiment may not necessarily be due to the presence of a reduced species of Ru(bpy)$_2^{2+}$ which was the expected result. It may be that the spectrum in Figure 12B is indicative of an intermediate species. It is also possible that the reduced species is not adsorbed and the spectrum in Figure 12B is of Ru(bpy)$_2^{2+}$, the spectral changes being merely due to the very negative potential of the electrode.

**Spectral Differences between Ru(bpy)$_2^{2+}$ on Ag and Ag/GaAs.**

In ref 1 we touched upon the subject of spectral differences observed between Ru(bpy)$_2^{2+}$ adsorbed on Ag and Ru(bpy)$_2^{2+}$ adsorbed on GaAs with Ag overlayer. It should be noted that SERRS spectra of Ru(bpy)$_2^{2+}$ on Ag are virtually indistinguishable from RR spectra of Ru(bpy)$_2^{2+}$ in solution except for a fluorescence background which appears in the solution spectrum with 457.9-nm excitation. A comparison of SERRS spectra of Ru(bpy)$_2^{2+}$ on Ag and on Ag/GaAs shows only very subtle differences. The modes which are the most dissimilar are the same which showed changes in the experiment depicted in Figure 12. Figure 13 highlights these bands, showing partial SERRS for Ru(bpy)$_2^{2+}$ on Ag and Ru(bpy)$_2^{2+}$ on GaAs with a Ag overlayer (Ag/GaAs). Spectral differences are more pronounced in SERRS spectra excited at 514.5 nm than at 457.9 nm. In fact, the differences observed in the 1000-1100-cm$^{-1}$ region for Ag and Ag/GaAs at 514.5 nm are very similar to differences observed for SERRS spectra of Ru(bpy)$_2^{2+}$ on Ag at 514.5 and 457.9 nm, respectively. Although the Ag spectrum in Figure 13 shows a very small shoulder on the 1496-cm$^{-1}$ band, this shoulder is very much enlarged on the Ag/GaAs spectrum. Also, the bandwidths for the Ag/GaAs spectra are broadened by ca. 30%. The large shoulder on the 1496-cm$^{-1}$ band in the Ag/GaAs spectrum is reminiscent of that in Figure 12B. It may be that the general broadening of the bands in the Ag/GaAs spectrum is due to a greater variety of adsorption sites on this surface. The shoulder on the 1496-cm$^{-1}$ band may arise from molecules adsorbed at very negative potentials of it may be that such negative sites do indeed exist, they may be associated with carbon or oxide contamination of the GaAs surface as the shoulder on the 1496-cm$^{-1}$ band seems more prominent in spectra which show evidence of C and O contamination.

Because the spectral differences between Ag and Ag/GaAs surfaces are so subtle, it is not possible to say unequivocally that the SERRS signal arises from molecules adsorbed to GaAs.

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SERRS of Adsorbates on Semiconductor Electrode Surfaces

Figure 14. Illustration of possible SERRS-active sites.

is possible that Ru(bpy)$_2^{2+}$ molecules adsorbed to GaAs desorb and then the adsorb to Ag when Ag is deposited electrochemically. In the next section we address the issue of the most probable location of the SERRS molecules with respect to the Ag islands.

The Location of "SERRS-Active Molecules" with respect to Ag Islands on Ag Modified SC Surfaces. The position of the "SERRS-active molecules" with respect to the Ag islands is very important to determine from the standpoint of both SERRS and photoelectrochemical research. It is a crucial piece of information as far as understanding SERRS mechanisms is concerned, and the application of SERRS to studies of reactions at SC electrode surfaces will be of value only if scattering from molecules adsorbed on the SC surface is enhanced. Unfortunately, the determination of the location of the SERRS molecules appears to be a very nontrivial task. Direct spectral information is somewhat ambiguous for the Ag/GaAs/Ru(bpy)$_2^{2+}$ system. Although all the electrodes in this study were treated with Ru(bpy)$_2^{2+}$ before Ag was deposited, it is not a certainty that the Ru(bpy)$_2^{2+}$ has remained adsorbed to GaAs after Ag is deposited. Consider the possible locations of the "SERRS-active molecule" depicted in Figure 14. At least four adsorption environments classified by the direct interactions of the "SERRS molecule" can be conceptually identified: (1) contact with GaS and solution, (2) contact with GaAs and Ag (at interface between phases), (3) contact with Ag only (incorporated into Ag island), and (4) contact with Ag and solution (a situation which would involve desorption from GaAs and adsorption onto Ag during deposition). It should be noted that a variety of SERRS sites may be the reason for the general broadening of spectral features for Ru(bpy)$_2^{2+}$ on Ag/GaAs.

Let us examine each category with regard to its probability. Category I is, without a doubt, present for all Ag/GaAs/Ru(bpy)$_2^{2+}$ electrodes studied in this work. How intense the SERRS signal is from molecules at this position will depend on their distance from the Ag particles as predicted by the electromagnetic SERS theories. Position 2 is also likely to exist on our Ag/GaAs/Ru(bpy)$_2^{2+}$ surfaces—particularly if Ag deposits initially at sites already occupied by Ru(bpy)$_2^{2+}$. This seems quite likely especially if Ru(bpy)$_2^{2+}$ is coadsorbed on GaAs with Cl-. Positions 3 and 4 are less likely to be operative in our experiments but may be present as a small percentage of the SERRS sites in some experiments. These sites would require that Ru(bpy)$_2^{2+}$ desorb from GaAs during Ag deposition. Category 3 is probably the least likely of the four since it would necessitate incorporation of Ru(bpy)$_2^{2+}$ and its counterions into the Ag lattice. Category 4 is probably not operative in cases in which Ag is deposited on GaAs/Ru(bpy)$_2^{2+}$ and then partially stripped. Experiments in which Ag was deposited in cases in which Ag is deposited on GaAs/Ru(bpy)$_2^{2+}$ and then partially stripped. Experiments in which Ag was deposited in this manner resulted in spectra of comparable or improved intensity relative to spectra of electrodes for which Ag was deposited in the usual manner. Thus, it can be concluded that position 4 contributes very little to our SERS signals. Since intense in situ spectra of Ru(bpy)$_2^{2+}$ on Ag/GaAs are obtained at -2.8 V vs. Ag/Ag$^+$ (0.01 M), a potential at which reduced Ru(bpy)$_2^{2+}$ is expected to desorb, it seems likely that position 2 contributes considerably to the signal. Of course, category 1 is the most desirable SERRS site since this type of site is required in order to monitor dynamic photoelectrochemical processes with SERRS.

Conclusion

The work presented in this paper constitutes a promising start toward two major goals of this research: (1) the realization of in situ monitoring of dynamic processes on SC electrodes with monolayer sensitivity using SERRS and (2) the compilation of information about SERRS phenomena associated with adsorbates on semiconductor substrates with SERS metal overlayers. As is the case with most new research efforts, our initial results generate more questions than answers. However, the value of the SERRS overlayer technique to the study of SC electrode surfaces is clear. Adsorbates are detectable with excellent molecular specificity at submonolayer coverages on SC electrode surfaces.

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Registry No. Fe(bpy)$_2^{2+}$, 15025-74-8; Ru(bpy)$_2^{2+}$, 15158-62-0; Fe(phen)$_2^{2+}$, 14708-99-7; GaAs, 1303-00-0; Ag, 7440-22-4; Si, 7440-21-3.