

Observation of Molecules Adsorbed on III-V Semiconductor Quantum Dots by Surface-Enhanced Raman Scattering

Lucia G. Quagliano*

Contribution from the Institute for Nanostructured Materials (ISMN), Consiglio Nazionale delle Ricerche (C.N.R.), Area della Ricerca di Roma 1, P.O. Box 10, 00016 Monterotondo Scalo (Roma), Italy

Received December 11, 2003; E-mail: lucia.quagliano@mliib.cnr.it

Abstract: I report for the first time surface-enhanced Raman scattering (SERS) from molecules adsorbed on InAs/GaAs quantum dots. This result is very interesting because previous SERS experiments have been essentially restricted to molecules adsorbed on metallic surfaces. Raman scattering from pyridine molecules adsorbed on these III–V quantum dots structures is strongly enhanced relative to the same molecules in solution. The most interesting feature in the SERS spectrum is the appearance of a new vibrational band. I suggest that this line should be attributed to the chemisorbed pyridine that is formed by coordination of its lone pair electrons of the N atom to the semiconductor surface. This work provides unambiguous experimental evidence for SERS on III–V semiconductor quantum dots. Nanostructures are currently considered as potential building blocks for nanodevices. The performance and reliability of these devices strongly depend on the surface and interfacial properties of the constituent nanomaterials. Therefore, this work illustrates the considerable potential of SERS spectroscopy as a powerful new tool in nanoscience.

1. Introduction

This is the first study in which surface-enhanced Raman scattering (SERS) has been used to directly probe the adsorption of molecules on III–V semiconductor quantum dots nanostructures. Utilizing SERS spectroscopy, I improved the Raman signal by several orders of magnitude and obtained an extremely high sensitivity to probe interfaces.

The SERS effect is characterized by an increase in the Raman intensity by many orders of magnitude for species adsorbed on rough metal surfaces with respect to that expected from the same number of nonadsorbed molecules, in solution or the gas phase.^{1–12} Until now, SERS experiments have been essentially restricted to adsorbates on rough metallic surfaces prepared by various methods, especially noble and alkali metals. A necessary, but not sufficient, requirement for the presence of high surface enhancement is some form of surface roughness. Recently, interest in the SERS spectroscopy has been stimulated by the

detection of a single molecule^{13–14} that will open new horizons for biophysical and biomedical fields.

For semiconductor materials, conventional Raman spectroscopy is a poor technique for examining surface and interfacial species present at low concentration. The use of SERS may render possible or facilitate Raman studies. As surface spectroscopy, the SERS technique has a number of important advantages: sensitivity, selectivity, nondestructive detection, and feasibility for in situ studies. Besides, this spectroscopy enables the determination of detailed information about adsorbed species such as their molecular structure and orientation.

In my past work,^{15–16} I showed that by depositing silver nanoparticles on semiconductor materials it was possible to detect adsorbates. Applying this method to several semiconductors, Si, GaAs, InAs, and InP, I observed the presence of adsorbed species. More recently, by means of this Ag-overlayer technique I observed Raman bands of contaminants present at low concentration on the semiconductor surface, augmented through the surface-enhanced scattering mechanism.

Motivated by these developments concerning the ability of the SERS technique to detect surface species, contaminants, and adsorbates by using the Ag-overlayer technique and by the SERS sensitivity to very small amounts of material, I have become interested in the application of SERS technique for studying technologically important materials, like semiconductor quantum dots. In recent years, interest has grown in semiconductor

- (1) Chang, R. K.; Furtak, T. E. *Surface Enhanced Raman Scattering*; Plenum: New York, 1982.
- (2) Otto, A. In *Light Scattering in Solids IV*; Cardona, M., Guentherodt, G., Eds.; Topic in Applied Optics; Springer: Heidelberg, 1984; p 289.
- (3) Van Duyne, R. P. In *Chemical and Biochemical Applications of Lasers*; Moore, C. B., Ed.; Academic Press: New York, 197; Vol. 4, pp 101–184.
- (4) Moskovits, M. *Rev. Mod. Phys.* **1985**, *57*, 783–826.
- (5) Lombardi, J. R.; Birke, R. L.; Lu, T.; Xu, J. *J. Chem. Phys.* **1986**, *84*, 4174–4180.
- (6) Schlegel, V. L.; Cotton, T. M. *Anal. Chem.* **1991**, *63*, 241.
- (7) Champion, A.; Kambhampati, P. *Chem. Soc. Rev.* **1998**, *27*, 241–250.
- (8) Tian, Z. Q. *Internet J. Vib. Spectrosc.* **2000**, *4*, 2. <http://www.ijvs.com>.
- (9) Otto, A. *Phys. Status Solidi A* **2001**, *188*, 1455–1470.
- (10) Moskovits, M.; Tay, L. L.; Yang, J.; Haslett, T. *Top. Appl. Phys.* **2002**, *82*, 215.
- (11) Weaver, M. J.; Zou, S.; Chan H. Y. H. *Anal. Chem.* **2000**, *72*, 38A–47A.
- (12) Tian, Z. Q.; Ren, B.; Wu, D. Y. *J. Phys. Chem. B* **2002**, *106*, 9463–9483.

- (13) Nie, S. M.; Emory, S. R. *Science* **1997**, *275*, 1102–1106.
- (14) Kneipp, K.; Wang, Y.; Kneipp, H.; Perelman, L. T.; Itzkan, I.; Dasari, R. R.; Feld, M. S. *Phys. Rev. Lett.* **1997**, *78*, 1667–1670.
- (15) Quagliano, L. G.; Jusserand, B.; Orani, D. *J. Raman Spectrosc.* **1998**, *29*, 721–724.
- (16) Quagliano, L. G. *Internet J. Vib. Spectrosc.* **2000**, *4*, 3. <http://www.ijvs.com>.

structures with reduced dimensionalities due to their novel properties related to quantum confinement as well as their promising device potentialities. For this reason, I have decided to investigate nanostructures of semiconductors such as InAs/GaAs quantum dots.

In this work, I present an extension of the SERS effect to semiconductor surfaces providing unambiguous evidence for SERS from III–V semiconductor quantum dots. Using pyridine as test molecule, I observed, for the first time, surface-enhanced Raman scattering from InAs/GaAs quantum dots. Pyridine has been chosen as the probe molecule because its Raman spectrum is sensitive to the environment of the molecule.

One interesting feature in the SERS spectrum of pyridine adsorbed on these semiconductor nanostructures is the appearance of a new band. The observation of new bands indicates a strong interaction between the adsorbate and the semiconductor atoms. The appearance of this relatively intense band is probably due to the chemisorbed pyridine that is formed by coordination of its lone pair electrons of the N atom to the semiconductor surface.

I estimate a large surface enhancement factor of the order of 10^3 for this quantum dots system. This represents an enormously enhanced Raman cross section compared to the intensity expected from the same number of nonadsorbed molecules. This suggests that the Raman signals measured on the semiconductor nanostructure originate from pyridine molecules adsorbed on it, and I was able to observe them because they are enhanced through the SERS effect.

One promising application of the SERS technique could be research on the integration of inorganic, organic, and biological nanostructures to build novel functional systems. Recently, the functionalization of semiconductor surfaces through chemisorption of organic molecules has generated much interest because of its potential applications in molecule-based devices and biosensors. There is currently great interest in creating extremely sensitive and specific chemical and biological nanosensors. In this regard, the interaction between biological, organic, and inorganic materials surface will be one of the key issues soon. The use of an extremely sensitive technique such as SERS spectroscopy to study organic–inorganic interconnections, including interfacing to biological systems, permitted us to investigate the role of interfaces in hybrid electrical devices and sensors. Therefore, my extension of the SERS technique as a new method to characterize the structure and composition of surfaces and interfaces in semiconductor quantum dots is important for developing SERS as a powerful tool in nanoscience.

2. Experimental Section

Self-assembled InAs/GaAs quantum dots grown by molecular beam epitaxy,¹⁷ GaAs, and InAs (wafers and epitaxial layers) were utilized. The quantum dots nanostructures were not covered with a cap layer. To obtain the adsorption of pyridine, the samples were immersed in liquid pyridine for at least 15 min. At the end of these treatments, the samples were rinsed in acetonitrile (ACN) and subjected to a short ultrasonic agitation in ACN to remove excess species, so that only adsorbed species were left on the surfaces. Commercially available pyridine was used.

The Raman measurements were performed with a triple spectrometer Dilor XY, equipped with a cooled CCD detector, in conjunction with a confocal microscope. A 10× objective was used to focus the laser light on the samples and to collect the Raman signal. The excitation light was the 514.5 nm line of an argon ion laser.

3. Results and Discussion

In recent years, there has been a growing interest in semiconductor structures with reduced dimensionalities because of their novel properties related to quantum confinement as well as their promising device potentialities. For this reason, I decided to investigate nanostructures of semiconductors such as self-assembled InAs/GaAs quantum dots.

Strain plays a crucial role in the process of quantum dots formation, providing a natural driving force, which causes the transition from two-dimensional to three-dimensional growth mode, i.e., the formation of islands. When InAs is grown on the GaAs substrate because of the large lattice mismatch between these two materials, InAs islands are formed. There are two stages in this growth. At the beginning the InAs grows two-dimensionally, although the InAs suffers compressive strain. When exceeding a certain InAs thickness, the strain becomes large and a morphological phase transformation occurs, which results in the formation of three-dimensional InAs islands.

The nanostructures were grown without cap layer; usually the cap layer is grown to perform photoluminescence experiments. As shown by atomic force microscope (AFM) images, the InAs/GaAs quantum dots consist of homogeneous InAs islands formed on GaAs with a mean diameter of about 40 nm, a height of 10 nm, and an average distance between the islands of about 60 nm. This surface is rather uniform; therefore, I believed it could be suitable as SERS surface.

3.1. Adsorption of Pyridine Molecules on InAs/GaAs Quantum Dots. A pyridine molecule (C_5H_5N) was chosen for this investigation since it has been used in many SERS studies because of the strength of the Raman signal and the sensitivity of its spectral features to the local environment. In fact, some lines of pyridine are sensitive to the environment of the molecule, so that by using Raman spectroscopy it is possible to distinguish between different adsorption sites. In pyridine, both the lone pair of electrons on the N-atom and the delocalized π -system of electrons enable various interactions with surface atoms, and changes in the Raman vibrational frequencies provide information to the molecule–substrate interaction.

Figure 1 shows the ex situ Raman spectrum from InAs/GaAs quantum dots after the immersion in liquid pyridine and the following sonication. This spectrum, recorded in air, consists of many peaks. The most intense lines are located at 1010 and 1045 cm^{-1} along with a band at 1032 cm^{-1} ; weaker ones are at 627, 658, and 724 cm^{-1} . A strong background underlies the peaks; this is due to the semiconductor overtone and combination bands.^{18,19} As a matter of fact, I also observed this background in the Raman spectrum of the InAs/GaAs quantum dots before immersion. I observed no vibrational bands from oxides.

I also measured the Raman spectrum of liquid pyridine and observed a close resemblance between this spectrum and that in Figure 1. This suggests that the Raman signals measured on

(17) Gerard, J. M.; Marzin, J. Y.; Zimmermann, G.; Ponchet, A.; Cabrol, O.; Barrier, D.; Jusserand, B.; Sermage, B. *Solid-State Electron.* **1996**, *40*, 807–810.

(18) Trallero-Giner, C. *Phys. Status Solidi B* **2004**, *241*, 572–578.

(19) Klein, M. C.; Hache, F.; Ricard, D.; Flytzanis, C. *Phys. Rev. B* **1990**, *42*, 11123–11132.

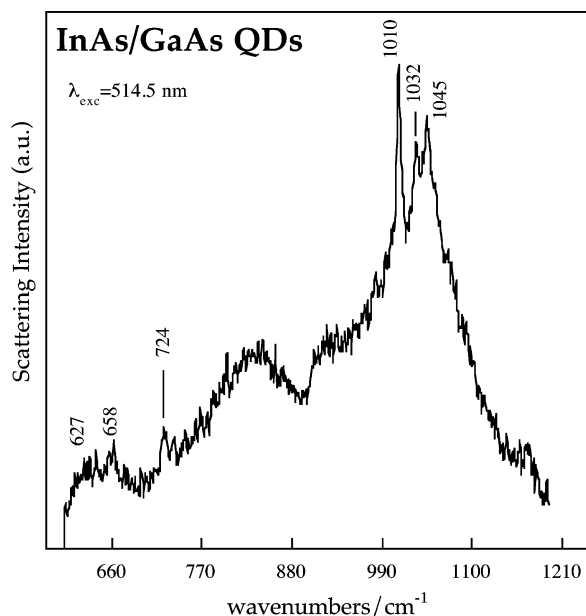


Figure 1. SERS spectrum of pyridine adsorbed on InAs/GaAs quantum dots nanostructure.

the semiconductor nanostructure originate from pyridine molecules adsorbed on it, and I was able to see them because they are enhanced from the SERS effect.

Details of band positions and tentative assignments are tabulated in Table 1, together with my Raman data of liquid pyridine. The notation of Wilson is followed.²⁰ Literature data for SERS spectra of pyridine adsorbed on various systems are also reported.

From the spectral positions of the observed features, I can affirm that there is only a monolayer of pyridine adsorbed on the semiconductor nanostructure. As a matter of fact, vibrational energies of surface pyridine are generally shifted to higher values with respect to corresponding vibrations from “bulk” pyridine, i.e., pyridine in the second and consecutive layers.

To ascribe the SERS spectrum of pyridine adsorbed on InAs/GaAs quantum dots to an appropriate form of adsorbed pyridine, I compared this spectrum with the SERS spectra of pyridine adsorbed on various metal surfaces prepared by various methods reported in the literature. A comparison with the SERS spectra of pyridine adsorbed on silver surface, which is the most studied SERS system, shows that this spectrum is quite similar to these spectra. In the SERS spectrum of pyridine adsorbed on Ag surface, the strongest bands, assigned to ring-breathing vibrations, appear at 1010 (ν_1) and 1036 (ν_{12}) cm^{-1} . Sometimes for pyridine molecules adsorbed on silver electrode immersed in aqueous electrolytic solution an additional Raman band appears at 1025 cm^{-1} . The origin of this band, which is absent in the Raman spectrum of free pyridine, is still uncertain. It appeared in some reports and was not observed in others.

Fleishmann et al.²¹ observed this band in neutral solution and suggested that it is associated with pyridine coordinated to the Ag electrode through the nitrogen atom. Many investigations have been performed in acid solution, and it has been proposed that this band is due to pyridinium ion or pyridinium chloride

adsorbed on the silver electrode. Summarizing the results of these investigations on silver electrode I can conclude that for the band at 1025 cm^{-1} two explanations are possible. In neutral and basic solution, the formation of Lewis acid bonds between silver and pyridine is responsible for the appearance of this line, whereas in acid solution this is due to the pyridinium ion. The appearance of this band was also reported for pyridine adsorbed on Cu_2O surface by Kudelski et al.²² They affirmed that on such surfaces pyridine molecules adsorb as pyridinium cations.

Tian and co-workers^{23,24} investigated systematically the surface Raman spectra of pyridine on various coinage and transition-metal surfaces. They observed metal-dependent spectra. For the coinage metals they observed that the band for the ν_1 mode shifts from 1007 cm^{-1} on the silver surface to 1012 and 1017 cm^{-1} for pyridine on gold and copper surfaces, respectively, whereas for the transition metals the frequency of the ν_1 band changed from 1001 cm^{-1} on Pd to 1015 cm^{-1} on Pt. Besides the difference in frequency, they also observed different relative intensities from some bands depending on the different metals and attributed these features to the different orientation on the different surfaces. The ν_{10} band is very strong for free pyridine and also at the silver surface. However, it is very weak at gold and copper and has almost vanished at the Pt surface. Feilchenfeld et al.²⁵ also observed changes in the frequency positions for pyridine adsorbed on rhodium films deposited on silver electrodes. They observed intense ν_1 and ν_{12} vibrational modes at 1020 and 1046 cm^{-1} , respectively. It is clear from these studies that both the frequencies and relative intensities of SERS spectra can vary considerably with the nature of the substrate.

In the SERS spectrum from InAs/GaAs quantum dots reported in Figure 1, the two prominent bands at 1010 and 1045 cm^{-1} may be assigned to the symmetric ring-breathing vibration modes ν_1 and ν_{12} of adsorbed pyridine, respectively. The vibrational frequency of the ν_1 mode slightly shifts with respect to that of pyridine adsorbed on silver surface. The band frequency for the ν_{12} mode at 1045 cm^{-1} is higher than that on the silver and gold surface, at 1036 and 1038 cm^{-1} respectively, but is almost that of the ν_{12} vibrational mode of pyridine adsorbed on the rhodium–silver system.²⁵ Therefore, these frequency shifts are reasonably attributable to the substantially different behavior of adsorbed pyridine on the different solid surfaces.

It should be noted that between the two strongest peaks there is another intense one at 1032 cm^{-1} . I can associate this peak with the 1025 cm^{-1} band that has sometimes been detected on pyridine adsorbed on silver electrode surface, shifted to higher energy by 7 cm^{-1} with respect to the silver surface. For the Ag electrode, this band is associated with pyridine coordinated to the silver through the nitrogen atom.

Pyridine is a strong electron donor because of the existence of a lone pair of electrons on the nitrogen atom. The surface of the InAs/GaAs quantum dots nanostructure is probably an arsenic-stabilized surface (As-rich condition). Therefore, I can

(20) Long, D. A.; Murfin, F. S.; Thomas, E. L. *Trans. Faraday Soc.* **1963**, *59*, 12.

(21) Fleishmann, M.; Hendra, P. J.; McQuillan, A. J. *Chem. Phys. Lett.* **1974**, *26*, 163–166.

(22) Kudelski, A.; Grochala, W.; Janik-Czachor, M.; Bukowska, J.; Szummer, A.; Dolata M. J. *Raman Spectrosc.* **1998**, *29*, 431–435.

(23) Tian, Z. Q.; Gao, J. S.; Li, X. Q.; Ren, B.; Huang, Q. J.; Cai, W. B.; Liu, F. M.; Mao, B. W. *J. Raman Spectrosc.* **1998**, *29*, 703–711.

(24) Wu, D. Y.; Ren, B.; Jiang, Y. X.; Xu, X.; Tian, Z. Q. *J. Phys. Chem. A* **2002**, *106*, 9042–9052.

(25) Feilchenfeld, H.; Gao, X.; Weaver, M. J. *Chem. Phys. Lett.* **1989**, *161*, 321–326.

Table 1. Vibrations of Pyridine (Py) in Various Systems (in wavenumbers/cm⁻¹)

mode ^a	liquid Py ^b	SERS from InAs/GaAs Quantum-Dots ^c	SERS from Ag electrode ^d	SERS from Ag film ^e	SERS from Au ^f	SERS from Cu ^g	SERS from Pt ^h	SERS from Ag/Rh ⁱ	SERS from Cu ₂ O ^j
ν_{6a}	605	627	625				642	646	
ν_{6b}	652	658	654						
ν_{11}	700	724							
ν_1	991	1010	1006	1010	1012	1017	1015	1020	1005
		1032	1025						1024
ν_{12}	1029	1045	1034	1036	1038	1042		1046	

^a Assignments, after ref 20. ^b Liquid pyridine, my measurements. ^c Py on InAs/GaAs quantum dots, my measurements. ^d Py on Ag electrode, after ref 21. ^e Py on Ag film in UHV, after refs 26 and 27. ^f Py on Au electrodes, after refs 23 and 24. ^g Py on Cu electrodes, after refs 23 and 24. ^h Py on Pt electrodes, after refs 23 and 24. ⁱ Py on Ag electrode modified by rhodium film, after ref 25. ^j Py on Cu₂O hydrosol, after ref 22.

suppose that when pyridine molecules adsorb on our III–V nanostructure, their electrons are very likely trapped by the electron-deficient atoms of arsenic. I suggest that the relatively intense band at 1032 cm⁻¹ should be attributed to the chemisorbed pyridine that is formed by coordination of the lone pair electrons of the N atom of pyridine to the semiconductor surface. Recently, Cho et al.²⁸ investigated the adsorption of pyridine onto the Ge (100) surface by means of STM studies. They also found that pyridine molecules adsorb onto this semiconductor surface via the formation of Ge–N bonds through a Lewis acid-based reaction.

To ensure that the above features in the spectrum of InAs/GaAs quantum dots are due to the SERS effect, I measured the Raman spectrum of bare GaAs and InAs samples after immersion in pyridine and consecutive sonication. These spectra did not show any peaks except the characteristic ones from the semiconductor phonons, indicating that the Raman scattering from pyridine adsorbed on the quantum dots structure is surface-enhanced. However, only an extremely careful quantitative evaluation of the surface enhancement of the Raman scattering allows us to safely determine whether an observed weak Raman signal is surface-enhanced.

3.2 Evaluation of the Surface Enhancement Factor. To evaluate how strong the SERS effect is in the quantum dot structures, I have to estimate the surface enhancement factor (E_F). Namely, I have to compare the intensity of Raman scattering from molecules adsorbed on the nanostructure surface to the intensity expected from the same number of nonadsorbed molecules.

The surface-enhancement factor can be defined as:

$$E_F = (I_{\text{surf}}/N_{\text{surf}})/(I_{\text{free}}/N_{\text{free}}) = (I_{\text{surf}}/I_{\text{free}})(N_{\text{free}}/N_{\text{surf}}) \quad (1)$$

where I_{free} and I_{surf} are the experimental integrated intensities of the same band for free and adsorbed molecules, respectively, and N_{free} and N_{surf} are the number of free and adsorbed molecules taking part in the scattering process, respectively. Thus, the determination of the E_F requires that the spectra from adsorbed and free molecules be measured under identical conditions.

To obtain a quantitative evaluation of the surface enhancement factor, I performed a separate Raman experiment on the quantum dots structure in such a way that I was able to measure the number and the band intensities of adsorbed and nonad-

sorbed molecules directly under the same condition, taking advantage of the presence of an internal standard. For this purpose, I immersed the quantum dots sample in liquid pyridine, trying to keep the liquid level at the thickness of the collection volume. In the confocal configuration, the laser is focused on the sample with a microscope objective. Only signals from the volume very close to the focal point can be focused and reach the detector. As a matter of fact, the confocal Raman microscope defines in a precise way the volume from which the light is collected. A confocal system rejects out-of-focus light and off-axis light efficiently outside the sampling volume, and thus the detected intensity falls rapidly as the system is defocused. The lateral resolution together with the axial resolving power, or depth of focus, determines the analyzed volume. The lateral resolution is essentially determined by the diameter of the laser beam spot at $1/e^2$. The axial resolution is usually defined as the full width at half-maximum intensity. In the confocal experimental condition used, I can assume a lateral resolution ca. 10 μm and a depth of the focus ca. 1 μm .

With a thick pyridine liquid level I only observed the signal from pyridine. I can presume that in this case in the collection volume there is just the solution. At lower level, I measured the semiconductor signal as well as that from pyridine. I have to point out that in this condition I measured a lower signal from the phonon peaks of the semiconductor compared to that observed from the sample outside the pyridine. Decreasing the liquid level, I measured an increase of the semiconductor signal and almost the same counts from pyridine. Then, I slowly removed the liquid until I measured for the semiconductor almost the same counts obtained from the sample outside the liquid pyridine. I can suppose that in this condition the incident laser radiation was just at the semiconductor surface. Therefore, it is reasonable to assume the pyridine liquid level equal to the thickness of the collection volume, i.e., 1 μm . All pyridine molecules within the collection volume contribute to N_{free} . I am aware that this technique is not very accurate, but I would like to point out that in these conditions I estimate a lower limit of N_{free} . Therefore, at worst, I underestimate the surface enhancement factor (E_F).

The measured Raman spectrum in the range from 200 to 800 cm⁻¹ is shown in Figure 2. In this wavenumber region, I observed features characteristic of the semiconductor nanostructure as well as the pyridine molecules. The peak at 288 cm⁻¹ is due to the semiconductor quantum dots nanostructure; this band can be assigned to the GaAs longitudinal optical (LO) phonon mode. The peaks at 403, 601, 650, and 704 cm⁻¹ can be clearly assigned to pyridine bands; this Raman signal contains

(26) Yamada, H.; Yamamoto, Y. *Surf. Sci.* **1983**, *134*, 71–90.

(27) Yamada, H. In *Raman Spectroscopy: Sixty Years on Vibrational Spectra and Structure*; Bist, H. D., During, J. R., Sullivan, J. F., Eds.; Elsevier Science: Amsterdam, 1989; pp 391–406.

(28) Cho, Y. E.; Maeng, J. Y.; Kim, S.; Hong S. *J. Am. Chem. Soc.* **2003**, *125*, 7514–7515.

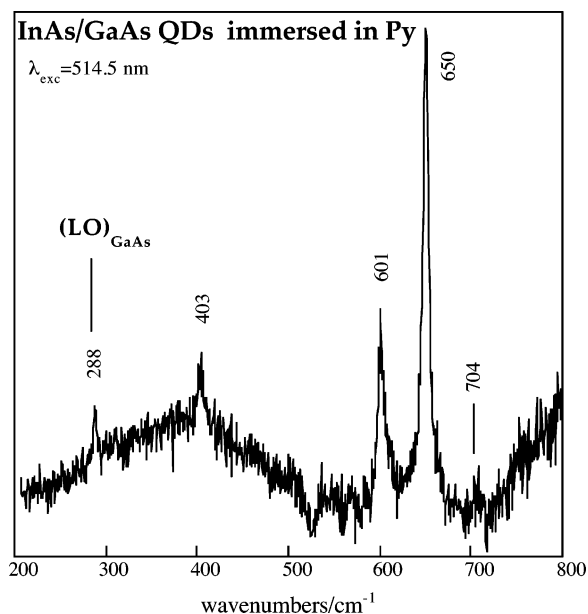


Figure 2. Raman spectrum of InAs/GaAs quantum dots nanostructure immersed in liquid pyridine.

contributions from pyridine molecules free and adsorbed on the semiconductor. It is likely that this signal comes almost completely from the liquid pyridine rather than the adsorbed molecules because the peak frequencies agree very well with those obtained from the Raman spectrum of liquid pyridine and the peak intensities are strongly increased with respect to those of pyridine adsorbed on the quantum dots structure.

To summarize, a comparison with the surface-enhanced Raman spectrum of pyridine presented in Figure 1 shows that in this unenhanced Raman spectrum the pyridine bands shift and increase strongly in intensity, while the Raman signal of the semiconductor nanostructure remains almost unchanged.

The surface enhancement of the Raman scattering can be expressed by the surface enhancement factor E_F . According to eq 1, E_F depends on the integrated intensities of the same band for adsorbed and nonadsorbed molecules as well as on the number of these molecules. To estimate the surface enhancement factor, I used the experimental scattering intensities of the ν_{6b} vibration mode of pyridine. The peak position of this mode for the adsorbed molecule is at 658 cm^{-1} (SERS spectrum in Figure 1), whereas for the free molecule it is at 650 cm^{-1} (unenhanced Raman spectrum in Figure 2). The SERS and Raman intensities of this band are related to an internal standard, such as the 288 cm^{-1} band from the quantum dot nanostructure. For the experimental integrated intensities I measured $(I_{\text{surf}}/I_{\text{free}}) = 4 \times 10^{-2}$.

Moreover, the determination of the E_F requires knowledge of the number of adsorbed (N_{surf}) and nonadsorbed (N_{free}) molecules effectively excited by the laser beam, namely, the molecules taking part in the scattering process. For this purpose, I have to estimate the scattering surface and volume. From the AFM images of the quantum dot sample I know the diameter, the height, and the interdistance of the InAs islands. By means of these values as well as of the spot laser diameter, I calculated a scattering area of 10^{-6} cm^2 . I would like to point out that this area is only 5% larger than the scattering area for a flat semiconductor surface. In fact, in the sample the surface roughness factor, defined as the area ratio of the real rough

surface to the ideally smooth surface, is almost 1. The evaluation of N_{surf} , carried out assuming the approximation for one monolayer adsorption, is 2.5×10^8 .

Taking advantage of the presence of the internal standard, I was able to evaluate the scattering volume. According to my previous assumptions, using the GaAs LO intensity as internal standard I estimated the pyridine liquid thickness equal to the thickness of the collection liquid volume, i.e., $1\text{ }\mu\text{m}$. As reported above, I would like to reiterate that with this assumption I underestimate the number of nonadsorbed molecules. Since all pyridine molecules within the illuminated liquid volume contribute to N_{free} , I determined that the effectively illuminated number of pyridine molecules in this experiment is 6×10^{14} . Thus, the enhancement factor E_F is estimated to be 10^3 .

This nominal enhancement factor is estimated, as usual, for a monolayer of adsorbed pyridine. From the frequency shift of the vibrational lines I concluded that there is only a monolayer of adsorbed material. On the other hand, the observed signal is mostly likely from a monolayer since the samples were washed in acetonitrile and sonicated and then examined in air. I emphasize that this surface enhancement factor of the order of 10^3 is large, and it definitely indicates the existence of the SERS effect on this III–V quantum dots structure.

Despite numerous theoretical investigations, a full understanding of SERS is still lacking. Several possible mechanisms of enhancement have been proposed. However, it is generally accepted that two main mechanisms contribute to the surface enhancement: the electromagnetic and the charge transfer.

The first attributes the enhancement to surface plasmon resonances of the metal, which enhance local electric fields at the surface. This effect is usually considered the most important, contributing about 10^4 of the total observed enhancement (commonly described as around 10^6) and is often called the physical effect, since all that is required is that the molecules are physisorbed at or near the surface. The second mechanism assumes that the incident photons cause a resonant charge transfer between the metal and the adsorbate with the formation of specific adsorbate–metal complexes. This produces an increase in the polarizability and then in the Raman scattering cross section of adsorbed species. However, applications of the charge-transfer theory usually can account only for about 10–100 of the observed enhancement factor.

Enormous enhancements with the surface enhancement factor up to 10^{14} have been reported in single molecule studies. Recently, huge surface enhancement factors have been observed by Van Duyne et al.²⁹ on nanostructured metallic substrates and by Gupta et al.³⁰ on tunable gold films with an enhancement factor on the order of 10^8 and 10^{11} , respectively. These SERS enhancements are mainly due to the optical properties of the metallic substrates that support surface plasmon excitation in the visible light region. Although the SERS observed signal would imply an enhancement factor of the order of 10^3 , the observed SERS spectra must be caused mainly by some other effect than the surface plasmon polaritons effect. This is because for III–V semiconductors the surface plasmon excitation resonance does not occur in the visible region but in the infrared, and therefore it is far from the used excitation wavelength.

(29) Haynes, C. L.; Van Duyne, R. P. *J. Phys. Chem. B* **2003**, *107*, 7426–7433.

(30) Gupta, R.; Weimar, W. A. *Chem. Phys. Lett.* **2003**, *374*, 302–306.

To understand the origin of the surface Raman enhancement in the semiconductor nanostructures, I have to consider the electronic properties of these kinds of surfaces and interfaces.

Since pyridine molecules observed in our SERS experiments adsorb strongly onto the quantum dots structure, a chemical enhancement could make an important contribution. As a matter of fact, the appearance of the relatively intense band at 1032 cm^{-1} ascribed to formation of Lewis acid bonds between pyridine and the semiconductor surface indicates that the molecule is chemically bonded to the surface.

Pyridine is a strong electron donor, and the lone pair of electrons on the nitrogen atom enables various interactions with surface atoms. The surface of the InAs/GaAs quantum dots nanostructure is probably an arsenic-stabilized surface. I may postulate that when pyridine molecules adsorb on the electron-deficient atoms of arsenic, these atoms on the semiconductor surface act as electron acceptors and combine to electron donors. Therefore, drawing from the charge transfer theory, in this semiconductor nanostructure the charge transfer can take place between filled adsorbate levels and empty semiconductor levels.

It is clear that considerably more research must be carried out to explain adequately the enhancement mechanism for SERS in semiconductor materials, which may be different from that of noble and transition metals. Thus, for a complete understanding of the SERS mechanism on semiconductors, theoretical studies as well as further experiments are required. I hope that the present work will stimulate these works.

4. Conclusions

This work is the first report on the SERS effect from molecules adsorbed on III–V semiconductor quantum dots. Until now, SERS experiments have been essentially restricted to adsorbates on rough metallic surfaces. Utilizing SERS spectroscopy, I improved the Raman signal by several orders

of magnitude and obtained an extremely high sensitivity to probe surfaces and interfaces. In the SERS spectrum a new band was detected, probably due to the interaction of pyridine with the semiconductor atoms via its nitrogen lone-pair electrons. The observation of this band indicates a strong interaction between the adsorbed molecules and the semiconductor atoms. I observed an enormously enhanced Raman cross section compared to the intensity expected from the same number of nonadsorbed molecules. This suggests that it is possible to study adsorption and reactions of molecules on the surfaces of III–V semiconductor quantum dots by means of SERS spectroscopy.

This work is important from the SERS point of view because it shows that semiconductor quantum dot structures are capable of supporting SERS. It is also important from the semiconductor's point of view since it shows that SERS investigation of surfaces and interfaces can be an important contribution to the analysis of semiconductor devices. Quantum dots are possible building blocks for novel nanodevices. The performance of these devices depends critically on the properties of the surface and interface features. It is therefore of interest to explore spectroscopic means of determining these properties. The successful SERS measurements on these semiconductor quantum dots suggest that SERS is a promising technique to investigate the integration of organic, inorganic, and biological nanostructures to build novel functional systems.

Acknowledgment. The author thanks J.-M. Gerard for providing the quantum dot structures. She also acknowledges J.-M. Moison for AFM investigations, B. Jusserand for useful discussion, and A. Otto and W. Richter for encouragement and advice. Part of this work was supported by the short-term mobility project of C.N.R.-Italy.

JA031640F