Surface-Enhanced Raman Scattering of Ultrathin Cadmium Chalcogenide Films on Gold Formed by Electrochemical Atomic-Layer Epitaxy: Thickness-Dependent Phonon Characteristics

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The utility of surface-enhanced Raman scattering (SERS) for characterizing phonon and related interfacial vibrations within ultrathin semiconductor layers on gold substrates is demonstrated, specifically for cadmium chalcogenide (CdSe, CdS) films formed by electrochemical atomic layer epitaxy. The occurrence of quantum-confinement effects for CdSe films less than ca. 10 monolayers thick is clearly evident from the observed ca. 12 cm^{-1} phonon redshifts and bandshape changes. Milder phonon redshifts are seen for the ultrathin CdS films, suggesting the presence of offsetting blueshifts from lattice compression. The observed sensitivity of the phonon spectra to the order of initial Cd/Se or Cd/S monolayer electrodeposition, along with the retention of Au−Se and Au−S vibrational bands upon layer growth, signal the importance of the initial chemisorbate to the epitaxial film structure and vibronic properties.

Introduction

Stimulated by the broad technological as well as fundamental significance of cadmium chalcogenide semiconductors, there is much interest in ambient chemical and electrochemical methods for preparing structurally well-defined films of these materials. One such strategy, pioneered and developed by Stickney and co-workers, is electrochemical atomic-layer epitaxy (ECALE).[1−3] This tactic exploits the well-known phenomenon of underpotential deposition (UPD) to yield uniform alternating electrodeposited layers of cadmium and chalcogenide on a noble-metal substrate. While the preparation of thick layers by ECALE desires automated flow-cell tactics,[3] an intriguing aspect of the approach is its intrinsic capability of forming uniform films even down to the monolayer level.[1,2] The structural integrity of such ultrathin films on gold electrodes has been demonstrated, in particular, by scanning tunneling microscopy (STM).[2,4,5] The layer-by-layer ECALE growth strategy also provides manifold opportunities to explore the thickness-dependent film optical properties, such as the lattice vibration (i.e., phonon) characteristics, by means of resonance Raman spectroscopy.[5,6] Indeed, this spectral technique has recently been utilized extensively to explore quantum confinement and related nanoscale structural effects in semiconductor thin films and particles.[7]

While resonance Raman spectroscopy can in suitable cases provide sufficient sensitivity to detect optical phonon modes even in ultrathin films,[5,7,8] vibrational characterization down to monolayer levels can be as challenging as it is desirable. For some time, we have been exploiting the excellent surface-enhanced Raman scattering (SERS) as well as electrochemical characteristics of gold substrates to obtain vibrational spectra for adsorbates on various ultrathin overlayer materials, especially transition metals, as well as for the films themselves, specifically for metal oxides, in electrochemical and ambient gaseous environments (e.g., refs 8−12). The suitability of this tactic for

examining UPD metal interfaces was demonstrated at the outset.[8] Prompted by the foregoing, we have recently been examining SERS of cadmium chalcogenide films and adsorbate modifiers on gold electrodes. While resonance-enhanced SERS has been utilized previously to examine phonon spectra for crystalline CdS bound to silver particles,[13] SERS studies of well-defined films are conspicuous by their absence. Some salient results for CdSe and CdS films are presented here. Besides demonstrating for the first time the overall virtues of SERS for characterizing such materials, the findings provide significant insight into quantum-confinement effects within uniform ultrathin films.

Experimental Section

Most experimental details for surface Raman spectroscopy are given in earlier reports.[11,14] The Raman excitation, from a Spectra Physics Stabilite model 2017 Kr$^+$ laser, was at 647.1 nm, with ca. 30 mW incident power on the sample surface. Scattered light was collected into a SPEX model 1877 Triplemate spectrometer, equipped with a Photometrics PM 512 CCD detector. The gold electrodes were 2 mm disks sheathed in Teflon. They were subjected to mechanical polishing with 1 and 0.3 μm Al_2O_3 powder successively, followed by a 5 min sonication. An electrochemical roughening procedure was employed to yield SERS activity, as outlined in ref 15. (Note that while the SERS-active surfaces contain arrays of ca. 100 nm gold particles,[15] the overall "roughness factors" are nonetheless small.[11])

The ECALE procedures for deposition of CdSe and CdS films on Au are essentially those described in refs 1b and 3. Specifically, the cadmium and chalcogenide layers were deposited alternatively in a pair of electrochemical cells. Cadmium UPD was carried out in either 10 mM $CdSO_4$ + 0.1 M Na_2SO_4 or 1 mM $CdSO_4$ + 0.1 M H_2SO_4 solutions at −0.65 and −0.4 V vs SCE, respectively. Selenium cathodic deposition was performed in 5 mM SeO_2 + 0.1 M $NaClO_4$ + 10 mM $Na_2B_4O_7$ at −0.95 V, and the corresponding sulfur layers were formed

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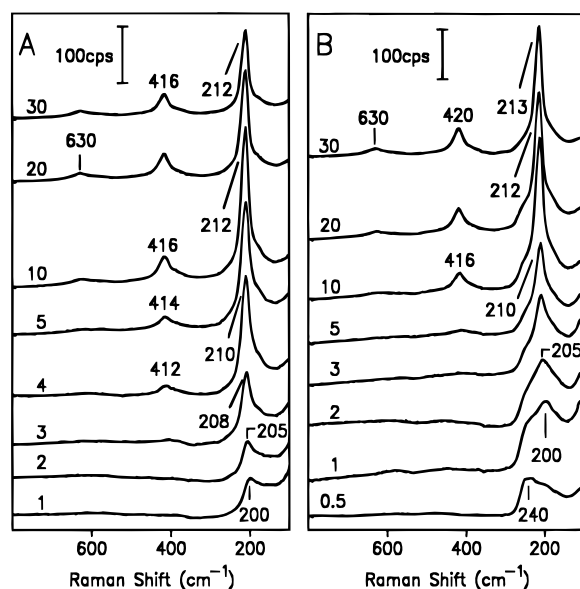
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Figure 1. Thickness-dependent SER spectra obtained at -0.6 V vs SCE for electrodeposited (A) Cd-first and (B) Se-first CdSe films on gold in 0.1 M NaClO$_4$ + 1 mM NaOH, with 20 s spectral acquisition time. The values alongside each spectrum refer to the thickness of deposited CdSe film in monolayers. See text for further details.

at -0.55 V in 10 mM Na$_2$S + 0.1 M NaClO$_4$ + 1 mM NaOH. The deposition time for each incremental monolayer step was 60 s. Upon completion of each step, the electrode was emersed under potential control and quickly rinsed with ultrapure water. The chemicals (mostly >99.99%) were obtained from Aldrich, and the solutions were prepared with ultrapure water from a Millipore MilliQ system. All measurements were performed at 23 ± 1 °C, and electrode potentials are reported versus a saturated calomel electrode (SCE).

Results and Discussion

Figure 1A shows representative SER spectra for progressively thicker CdSe films electrodeposited on gold, starting with the UPD cadmium monolayer, each acquired (20 s integration time) at -0.6 V vs SCE in 0.1 M NaClO$_4$ + 1 mM NaOH. Shown alongside in B is a corresponding sequence, obtained instead commencing with a selenium monolayer. (The values given beside each spectrum refer to the number of CdSe "monolayers", ML, so that the first Se layer alone is designated as "0.5 ML".) Clearly evident in both data sets is a sharp Raman band at 200 cm^{-1} which intensifies and blueshifts to 212 ± 1 cm^{-1} with increasing film thickness. This band can confidently be assigned on the basis of its frequency to the longitudinal optical (LO) phonon mode of CdSe, ν_{LO}, which appears at 210 cm^{-1} for "bulk" CdSe crystals at 300 K.[16] In addition to the fundamental LO mode, the first overtone at 410$-$420 cm^{-1} is evident by 4 ML in Figure 1A, with at least three overtones being discernible by 30 ML. The spectral appearance remained essentially unaltered within the electrode-potential range, -0.3 to -0.9 V, where the CdSe film is stable. The intensity ratio of the first overtone/fundamental bands increases from 0.12 to 0.4 between 4 and 30 ML, suggestive of a progressively larger electronic resonance involvement in the SER scattering. This finding is not surprising given that CdSe should yield near-band-edge light absorption (and hence the onset of resonance Raman scattering) at longer wavelengths for thicker films, resulting primarily from quantum-confinement effects on the band gap.[17] (Note that the excitation energy employed here, 1.92 eV, is larger than the

band gap for *bulk* CdSe, $E_g = 1.74$ eV at 300 K, although substantial increases in E_g are expected for the thin films examined here.[17])

Similar, although subtly different, vibrational characteristics are evident for CdSe films deposited instead commencing with the Se monolayer (Figure 1B). This initial step yields a broad feature at ca. 240 cm^{-1}, attributable to a surface-selenium stretching vibration, ν_{M-Se}, by comparison with SERS data for adsorbed sulfur and halides on gold electrodes.[14,18] (Note that the ν_{M-Se} frequency is similar to that anticipated from the latter data by presuming that the force constants of the surface bond with adsorbed S, Cl, and Br are comparable.[14,18]) Deposition of only one Cd monolayer on this Se adsorbate yields a phonon band at 200 cm^{-1} (Figure 1B), similar to that obtained for the first CdSe layer prepared with the deposition order reversed (Figure 1A). Subsequent CdSe deposition onto the "Se-first" template yields thickness-dependent phonon characteristics that are also closely comparable to those observed following initial "Cd-first" UPD (compare Figs. 1B with A). Thus, the LO phonon frequency blueshifts with increasing thickness towards a value, 212 cm^{-1}, close to that for bulk CdSe by ca. 10$-$15 ML, along with the appearance of at least two overtone bands, although the latter are clearly evident only for ≥ 10 ML in the Se-first case. Interestingly, however, a vestige of the ν_{M-Se} vibration remains as a high-frequency shoulder to the LO phonon fundamental for the Se-first films even up to 20 ML (Figure 1B), which is entirely absent for the Cd-first case (Figure 1A). This indicates that the substrate$-$Se bonding is retained in the epitaxial CdSe films (i.e., the initial Se layer remains intact upon film growth), even though their thickness-dependent phonon characteristics are insensitive to the Cd/Se deposition order.

The phonon mode softening observed for the ultrathin (≤ 10 ML) CdSe films is reminiscent of the well-studied quantum-confinement effects for CdSe nanoparticles.[19,20] Thus, LO phonon (ν_{LO}) redshifts of up to 10$-$12 cm^{-1} from the bulk behavior are observed for decreasing CdSe crystal diameters, $d \leq 5$ nm.[19,20] Given that each deposited CdSe monolayer is about 0.25 nm thick, the ν_{LO} film thickness dependence evident in Figures 1 A and B occurs over comparable spatial dimensions to the 3d quantum confinement effect studied extensively for CdSe nanoparticles.[19,20] The latter effect is due to phonon wavevector dispersion and, indeed, has been shown to be in approximate agreement with lattice dynamical predictions.[19a] Especially given that the LO phonon involves concerted lattice motion normal to the surface plane, the occurrence of a related quantum-confinement effect in the CdSe films appears to be reasonable. An accompanying phenomenon, shared to some extent by the CdSe nanoparticles and the present CdSe films, is phonon band broadening, evident in resonance Raman spectra for the former systems by a ν_{LO} low-frequency tail for particle diameters $d \leq 5$ nm, apparently arising from vibronic coupling.[19a] (Such bandshape changes, along with ν_{LO} redshifts, are indeed generally expected for ultrathin films as well as nanoscale rods and spheres, associated with phonon confinement.[21]) The bandwidth, $\Delta\nu_{1/2}$, for the thicker (≥ 10 ML) CdSe films is 18$-$20 cm^{-1}, rather broader than those reported for large (>5 nm) CdSe nanoparticles, ca. 8$-$10 cm^{-1}, at 300 K.[19,20] Nonetheless, a lower-frequency tail is increasingly evident for decreasing film thickness, $d \leq 2.5$ nm (Figure 1A and B), in a fashion similar to the CdSe nanoparticles. These trends therefore give us confidence that the thickness-dependent phonon characteristics observed here are also due chiefly to quantum-confinement effects.
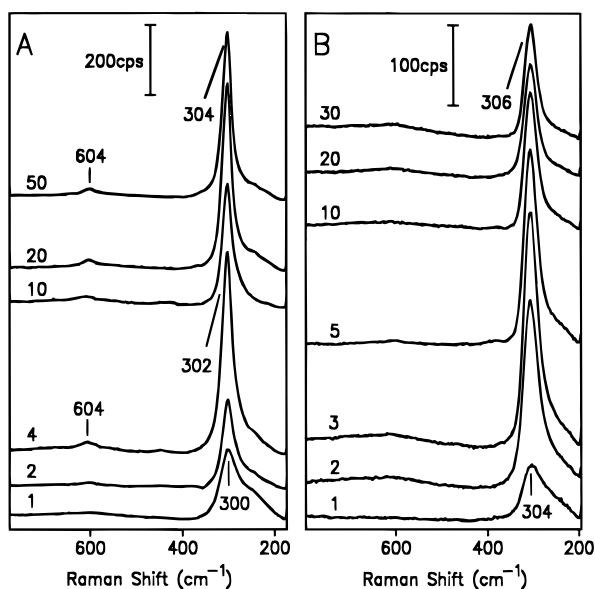
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Figure 2. Thickness-dependent SER spectra obtained at −0.6 V vs SCE for electrodeposited (A) Cd-first and (B) S-first CdS films on gold. See caption to Figure 1 and text for other details.

Figures 2 A and B show representative thickness-dependent SER spectra for CdS films electrodeposited on gold as noted above, also acquired at −0.6 V in 0.1 M $NaClO_4$ + 1 mM NaOH. Similarly to Figure 1, the A and B sequences refer to films formed by initial cadmium and sulfur monolayer deposition, respectively. Examining initially the Cd-first case (Figure 2A), an intense band at 300 cm^{-1} is evident even for a single CdS monolayer, which rapidly intensifies with increasing film thickness up to ca. 5 ML, eventually blue shifting slightly, to 304 ±1 cm^{-1}, for ≥10 ML. A weak overtone at 605 cm^{-1} is also present for the thicker films. The frequency of the former is consistent with that, 305 cm^{-1}, evaluated for the LO mode of bulk-phase (zinc blende) CdS crystals.[22]

The degree of ν_{LO} softening for the ultrathin CdS films (Figure 2A) is markedly smaller than that noted above for CdSe (Figure 1). Similarly small effects have also been observed for CdS nanocrystals,[23] even though significant (5−10 cm^{-1}) size-dependent ν_{LO} redshifts have been reported in some other studies.[24] The near-absence of a ν_{LO}-d dependence in the former case was attributed to the offsetting influence of phonon-confinement and "surface-tension" effects, which yield ν_{LO} red- and blueshifts, respectively, with decreasing particle size.[23] A related "compensation effect" is predicted if the initial ECALE deposition yields layers experiencing "compressive stress", since the ν_{LO} blueshifts thereby anticipated[21] would also offset the photon-confinement effect. Some evidence supporting this notion can be gleaned from the compressed lattice observed by STM for monolayer CdS deposition on Au(111) in comparison with the bulk-phase crystal dimensions.[5] For initial CdSe electrodeposition, on the other hand, such lattice stress/strain appears to be minimal,[2b,25] which would account for the apparently unfettered phonon-confinement effects in the CdSe films, as deduced from the ν_{LO} thickness dependence (vide supra). Similarly to the CdSe films, however, the CdS films exhibit a lower frequency tail that becomes more evident for d < 10 ML (Figure 2A). Comparable band shapes have been noted for smaller CdS nanoparticles, again indicative of a quantum-confinement effect.[23,24]

Somewhat similar SER spectra are evident for CdS films electrodeposited starting with a sulfur rather than a cadmium monolayer (Figure 2B). The S monolayer alone yields a broad feature at 300 cm^{-1}, assigned to metal surface−S stretching (ν_{M-S}). Addition of the first Cd layer is sufficient to yield a pronounced 304 cm^{-1} phonon peak astride the ν_{M-S} feature (bottom spectrum, Figure 2B). Further film growth atop the S-first template (Figure 2B) yields comparable phonon spectra to the Cd-first case (Figure 2A). However, at least two significant differences are apparent. First, the overtone at ca. 605 cm^{-1}, which is evident for the Cd-first case for $d \geq 2$ ML, is scarcely discernible even for the thickest (30 ML) S-first films. Second, the fundamental ν_{LO} band is distinctly narrower for the former films: for example, $\Delta\nu_{1/2} \approx 22$ and 30 cm^{-1} for the 30 ML Cd-first and S-first films, respectively. Some band narrowing for the latter films could be triggered by cycling the potential several times to and from the negative potential limit, −0.8 V, suggesting the occurrence of film restructuring. These findings therefore indicate that the CdS film structure is noticeably dependent on the nature of the initial chemisorbed layer.

Related results have been reported recently by Shannon and co-workers, who obtained resonance Raman spectra for CdS films grown by ECALE on ordered Au(111).[5] While the use of blue excitation lines produced strong resonance enhancement (enabling the ν_{LO} mode to be detected even for 4 ML films in the apparent absence of SERS), the S-first films yielded a broader ν_{LO} band and a weaker overtone feature.[5] Such spectral differences as for those observed here are indicative of a blue-shifted absorption band edge for the S-first CdS films, thereby yielding a weaker preresonance Raman effect than for the corresponding Cd-first films. The STM data also reported in ref 5 support the suggestion that these spectral differences are due to greater film "crystallinity" in the latter case. The markedly weaker overtone features seen in the present CdS SER spectra compared with the Raman results in ref 5 also indicate clearly that the former benefit little from resonance enhancement. This circumstance is expected since the band gap even for bulk CdS, 2.42 eV, is larger than the excitation energy (1.92 eV ≡ 647.1 nm) employed here.

A somewhat surprising aspect of the spectra in Figures 1 and 2 concerns the thickness-dependent band intensities. While the integrated intensities, I, of the phonon fundamental are only reproducible to within, say, 20−30%, due to the need to transfer the electrode to and from the deposition solutions, the $I-d$ profiles are not only nonlinear but nonmonotonic. While the details differ, the spectral sequences in Figures 1 and 2 all yield maximum ν_{LO} intensities for 3−10 ML. At least for localized vibrations, such as adsorbate intramolecular modes, the degree of Raman enhancement will decay with increasing spatial separation of the oscillator from the SERS-active substrate material.[11] Consequently, $I-d$ profiles associated with overlayer "lattice modes" should reach a plateau for thicker films, as indeed observed to occur for electrogenerated Cu_2O films, for example, by $d \geq 3$ nm.[26] While nonmonotonic Raman $I-d$ relations are generally expected for thin films from optical interferences, these effects appear only for $d \approx$ ca. 100 nm with visible radiation.[27] It is feasible that substrate−film charge-transfer contributions to the observed SERS enhancement effect could be partly responsible. More likely, however, the observed $I-d$ behavior reflects structural changes associated with film crystallinity.

Some measurements were conducted for cadmium chalcogenide films on polished gold substrates that did not undergo surface roughening. No detectable Raman signals were obtained using 647.1 nm excitation in this manner for CdS films, not surprisingly given that little or no resonance enhancement would

be expected. The CdSe films, however, yielded detectable Raman signals under these conditions, with similar spectral features to (yet ca. 10^2 fold weaker than) the SERS data in Figure 1. The spectra obtained in this fashion may nonetheless arise from some surface as well as resonance enhancement. It would be interesting to compare the thickness-dependent spectral properties for the same films under excitation conditions where either resonance or surface enhancement (i.e., SERS) is chiefly responsible for the Raman scattering.

The present results are considered to provide clear evidence of the heretofore unexploited virtues of SERS for revealing phonon and related adsorbate vibrations within thin semiconductor films in electrochemical systems, and by implication other ambient environments. The ability of the technique to readily achieve monolayer sensitivity (or below) even in the apparent absence of electronic resonance enhancement provides diverse opportunities for exploring quantum-confinement and other nano-/molecular-scale vibrational properties of such films in a fashion which is often difficult to achieve by other means.[28] For example, it should be feasible to scrutinize interfacial structure in composite thin films, such as superlattices and quantum wells formed from distinct semiconductor materials, with unique sensitivity and freedom from obfuscating lattice-specific resonance Raman effects. The SERS technique can be viewed as being complementary to resonance Raman spectroscopy, which has been utilized extensively to characterize thicker films in electrochemical[5,6,29] as well as gaseous environments. One virtue of SERS in comparison with conventional resonance Raman spectroscopy lies in the use of excitation radiation at energies well below those corresponding to the semiconductor band gap, thereby avoiding photocorrosion and other undesirable photochemical processes. The excellent temporal resolution afforded by the intense phonon SER signals also suggests its application as an "on-line" means of monitoring thin film characteristics during ECALE, in an analogous manner to Raman measurements performed during molecular-beam epitaxy.[30] Furthermore, the well-documented capability of SERS to provide rich *molecular* vibrational spectra for interfacial species should open up intriguing opportunities for exploring chemisorption and monolayer chemical modification of semiconductor thin films. Examinations along these lines are underway in our laboratory.

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