

## Communications to the Editor

### In-Situ Monitoring of Chemical Vapor Deposition at Ambient Pressure by Surface-Enhanced Raman Spectroscopy: Initial Growth of Tantalum(V) Oxide on Platinum

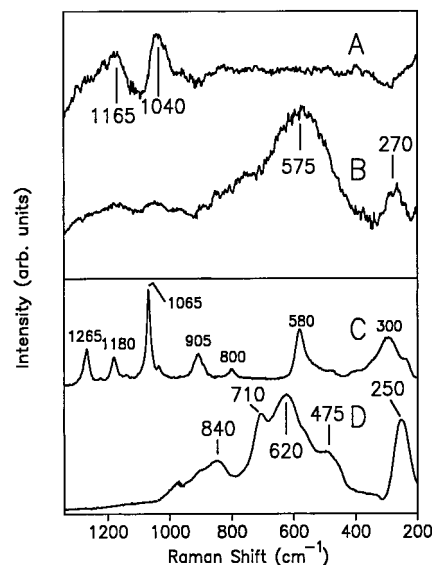
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Understanding the surface processes involved in the growth of solid-state materials by chemical vapor deposition (CVD) is of widespread interest given the considerable technological importance of processing nanoscale films having well-defined structure and composition.<sup>1</sup> The growth of such films has been investigated extensively by vibrational spectroscopy, chiefly by infrared reflection–absorption (IRAS) and electron energy loss (EELS) techniques in ultrahigh vacuum.<sup>2</sup> We report herein the utilization of surface-enhanced Raman spectroscopy (SERS) as an additional vibrational technique for characterizing the CVD process, applied specifically to the formation of tantalum(V) oxide films by the reaction of tantalum(V) ethoxide (“TaEtO”) precursor with dioxygen on a platinum substrate. Aside from the fundamental interest in elucidating the mechanism of this binary chemical process, Ta<sub>2</sub>O<sub>5</sub> has drawn considerable attention in the microelectronics industry recently since it is considered as the prime candidate among materials with high dielectric constant to replace SiO<sub>2</sub> as gate dielectrics and capacitors.<sup>3</sup> The results illustrate the heretofore unexploited potential of SERS for elucidating monolayer-level CVD processes under ambient-pressure conditions.

We have been interested for some time in extending the applicability of SERS for characterizing adsorption and related processes on a wide range of substrates, including Pt-group transition metals, by depositing them as ultrathin films onto a SERS-active gold template.<sup>4–7</sup> Recent advances have included the development of electrodeposition procedures for yielding essentially “pinhole-free” transition-metal films, enabling chemisorbate vibrational spectra to be obtained without chemical or spectral interferences from the underlying gold.<sup>5,6</sup> The large (10<sup>4</sup>–10<sup>5</sup> fold) surface Raman enhancement factors that are achieved for adsorbates on ultrathin (3–5 monolayer) Pt-group films on gold<sup>5b</sup> enable vibrational spectra to readily be obtained over wide frequency ranges with submonolayer sensitivity without bulk-



**Figure 1.** (A) Surface-enhanced Raman (SER) spectrum obtained upon exposing platinum film on gold to 100 cm<sup>3</sup> min<sup>-1</sup> of N<sub>2</sub> saturated with tantalum(V) ethoxide at 100 °C. (B) Ensuing SERS spectrum after flushing with N<sub>2</sub> and exposing to 100 cm<sup>3</sup> min<sup>-1</sup> of O<sub>2</sub> at 100 °C. (C) Raman spectrum of liquid tantalum(V) ethoxide. (D) Raman spectrum of Ta<sub>2</sub>O<sub>5</sub> powder.

phase interferences, even at ambient gas pressures and in electrochemical systems. The technique therefore offers unusual opportunities for the in-situ vibrational characterization of a variety of solid interfaces in ambient environments, including those of relevance to CVD processes. While other SERS strategies have been utilized recently to monitor the growth of diamond and silicon films,<sup>8</sup> the monolayer-level chemistry associated with binary CVD processes (such as Ta<sub>2</sub>O<sub>5</sub> formation) remains unexplored.

All SERS experiments in this study were performed in a stainless steel reactor, the configuration of which has been described elsewhere.<sup>7c</sup> Laser excitation was at 647.1 nm, with 30 mW incident on the sample, the scattered light being collected by a three-stage (Triplemate) spectrometer equipped with a CCD detector. The CVD substrate was an ultrathin (ca. 5 monolayers) Pt film electrodeposited on a polycrystalline gold foil. Details of the electrochemical procedures for SERS activation of gold and Pt film deposition can be found in refs 9 and 5a, respectively. The as-deposited Pt film was initially pretreated with H<sub>2</sub> in the reactor for 5 min at a substrate temperature of 100 °C. Tantalum(V) ethoxide (99.99%, Strem Chemicals) was delivered from a stainless steel bubbler using N<sub>2</sub> as the carrier gas. The temperature of the bubbler vessel, delivery lines, and reactor wall was held at 150 °C to avoid precursor condensation. All CVD experiments were performed under continuous flowing conditions at ca. 100 cm<sup>3</sup> min<sup>-1</sup> and atmospheric pressure.

To exploit the monolayer sensitivity of SERS to reveal the conversion from the adsorbed precursor to the desired film, we employed a deposition strategy that involves sequential dosing of the TaEtO and O<sub>2</sub> coreactant precursors, in principle allowing the film to be grown in a monolayer fashion.<sup>10</sup> This is in contrast to the conventional CVD procedure whereas both reactants are introduced simultaneously in which the film thickness is only controllable by adjusting the deposition time. Figure 1A displays

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the SER spectrum acquired upon dosing  $100 \text{ cm}^3 \text{ min}^{-1}$  of TaEtO-saturated  $\text{N}_2$  on Pt at  $100^\circ\text{C}$ . Two SERS bands are discernible immediately at  $1040$  and  $1165 \text{ cm}^{-1}$ . These features were retained after the reactor was flushed with pure  $\text{N}_2$  for 10 min to remove the gas-phase TaEtO. Subsequently dosing with  $\text{O}_2$ , however, yielded marked spectral changes. The resulting spectrum (Figure 1B) shows the disappearance of the  $1040$  and  $1165 \text{ cm}^{-1}$  SERS bands, and the advent of features at  $575$  and  $270 \text{ cm}^{-1}$ , the latter peaks growing in within 1–2 min.

The vibrational assignments are facilitated by comparison with the normal Raman spectra of liquid TaEtO as well as  $\text{Ta}_2\text{O}_5$  powder as shown in Figure 1, parts C and D, respectively. The broadness and ca.  $20 \text{ cm}^{-1}$  down-shift exhibited by the SERS features in Figure 1A upon comparison with the Raman bands of bulk TaEtO (Figure 1C) imply that the former originates from a chemisorbed form of ethoxide. While the Raman spectrum of liquid TaEtO has not apparently been analyzed in detail, it is similar to that of liquid ethanol.<sup>11</sup> The  $1040$  and  $1165 \text{ cm}^{-1}$  SERS features are tentatively correlated with the corresponding skeletal ethanol modes at  $1065$  and  $1180 \text{ cm}^{-1}$ , thereby providing evidence for nondissociated ethoxide adsorbate. These SER spectral features in Figure 1A are also reminiscent of published vibrational spectra of ethoxide adsorbed on transition metals.<sup>12</sup> At least on a qualitative level, then, ethoxide species are evidently chemisorbed on platinum, although it is not clear if there is Ta–ethoxide bond rupture.

Most significantly, the appearance of the broad SERS envelope around  $500$ – $600 \text{ cm}^{-1}$ , along with the  $270 \text{ cm}^{-1}$  features (Figure

1B), obtained upon subsequent  $\text{O}_2$  dosing at  $100^\circ\text{C}$  in relation to the bulk-phase  $\text{Ta}_2\text{O}_5$  spectrum (Figure 1D) provides strong evidence that the ethoxide precursor is being transformed into  $\text{Ta}_2\text{O}_5$  under these conditions. It is important to note that no such spectral features were obtained upon dosing  $\text{O}_2$  onto unmodified platinum at  $100^\circ\text{C}$ , heating to  $200^\circ\text{C}$  or above being required to form PtO at this surface.<sup>13</sup> Also, neither adsorbed ethoxide nor its oxidative conversion to  $\text{Ta}_2\text{O}_5$  were evident when performing parallel experiments on unmodified gold, no discernible SERS bands being obtained at either stage. This finding clearly implicates the chemisorbing role of platinum in assisting the oxidative formation of  $\text{Ta}_2\text{O}_5$ . It is plausible that the Pt substrate acts to “trap” the tantalum by triggering partial ethoxide ligand dissociation, yielding nonvolatile charged metal complexes. The inability of gold to incur such surface chemistry is unsurprising in view of its inert character.

Overall, the significance of the present study to the elucidation of CVD reaction pathways lies in the demonstration that SERS offers a versatile means of examining both precursor–substrate interactions and the initial transformation into a monolayer film.<sup>14</sup> Indeed, the present SERS results indicate that at least the initial deposition of  $\text{Ta}_2\text{O}_5$  on platinum can occur via a purely “surface” mechanism, thereby involving adsorbed precursor and oxidant. Consequently, the elementary chemical steps responsible for such binary CVD processes do not necessarily occur in the gas phase prior to deposition, but rather after one or both of the reactants is adsorbed. However, at present it is not clear that such a surface reaction as deduced here represents the dominant pathway under “technological” CVD conditions, whereby both the tantalum precursor and the oxidant are introduced together. Nevertheless, it is evident that the capability of imparting SERS activity to a variety of solid surfaces, achieved by ultrathin film deposition onto an inert gold template, provides broad-based opportunities for exploring the fundamental surface chemistry underlying processes of technological relevance, including microelectronic materials preparation.

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(14) Note also that SERS is intrinsically sensitive preferentially to the first few monolayers in the case where thicker films are formed.