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Chemical vapour deposition of selenium and tellurium films by UV laser photolysis of selenophene and tellurophene

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Excimer laser-induced photolysis of gaseous selenophene and tellurophene affords gaseous 1-buten-3-yne and ethyne (as major products) and butadiyne (a very minor product) and results in chemical vapour deposition of selenium and tellurium films. The film properties were characterized by XPS and SEM techniques and by UV spectroscopy. Copyright © 2000 John Wiley & Sons, Ltd.

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INTRODUCTION

Laser-induced chemical vapour deposition (CVD) of selenium and tellurium is of interest due to its importance for microelectronics, photographic imaging and metal–polymer optical storage media. Although various structurally different organoselenium and organotellurium compounds are available, gas-phase photolysis of these compounds has been only studied with R_2M (R = methyl, ethyl; M = Se, Te) compounds. Thus, photodeposition of selenium films from dimethylselenium[1,2] induced via radiation from Hg/Xe and Hg lamps is a very slow process due to low absorption in the precursor. Laser photolysis studied with 257 and 193 nm radiation related to substrate-adsorbed dialkyltellurium molecules;[3,4] Hg/Xe lamp- and laser-induced photolysis at 193 and 248 nm of gaseous R_2Te compounds yielded ground-state tellurium atoms and is suitable for photodeposition of tellurium films.[5–7]

The photolyses are hampered by hydrocarbon products which can be incorporated into the deposited films. These products may also act as surface inhibitors of film growth. The design of organoselenium or organotellurium precursors photolytically decomposed to selenium (tellurium) along with neutral and surface-non-interacting hydrocarbons is therefore of interest.

We have recently demonstrated deposition of tellurium and Te/C particles by excimer laser-induced photolysis of some organotellurium compounds, including tellurophene in the liquid phase.[8] We have also studied KrF laser photolysis of gaseous Et_2Te and Me_2Se and demonstrated their suitability for photodeposition of pure sub-micrometre particles of tellurium and of thin films of selenium which were not contaminated with hydrocarbon side-products (see also J. Pola, A. Ouchi, Z. Bastl and J. Šubrt, unpublished results).[9] In this paper we report on ArF and KrF laser photolysis of selenophene and tellurophene. We show that these processes are fast, yield non-obtrusive hydrocarbon products and afford pure thin films of selenium and tellurium.

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EXPERIMENTAL

Laser photolysis experiments were performed on gaseous samples of selenophene (2.7 kPa) and tellurophene (0.5 kPa) using a Lambda Physik LPX 210 i (ArF/KrF) laser operating with a repetition frequency of 10 Hz at 193 and 248 nm. The laser beam of different fluxes effective even an area of 2.6 cm^2 was measured by a Gentec ED-500 Joulemeter coupled with a Tektronix T912 10 MHz storage oscilloscope.

The samples of selenophene and tellurophene were irradiated in a Pyrex reactor consisting of two orthogonally positioned tubes (both 3 cm in diameter), one (13 cm long) furnished with KBr windows and the other (9 cm long) equipped with quartz windows. The reactor had two side arms, one fitted with a rubber septum and the other connecting it to a standard vacuum manifold. It accommodated metal, quartz and KBr substrates which, covered with solid material deposited in the course of photolysis, were transferred for measurements of their properties by UV spectroscopy, photoelectron spectroscopy and electron microscopy.

The procedure for the determination of depletion of the initial compounds and of the build-up of gaseous photolytic products has been described in detail elsewhere[10] and will be given here only briefly. The progress of the photolysis was monitored directly in the reactor by IR spectroscopy (a Shimadzu FTIR 4000 spectrometer) and, after expansion of helium into the reactor, also by GC (Gasukuro Kogyo model 370 chromatographs equipped with an I.D. Neutra Bond-1 capillary column 60 m long and a packed Unipak S SUS column 2 m long programmed temperature, helium carrier gas). The depletion of selenophene and tellurophene was followed by IR spectroscopy using diagnostic bands at 685 and 688 cm^{-1}, respectively and the photolytic products (ethyne, 1-buten-3-yne and buta-1,3-diyne) were monitored by both FTIR spectral and GC methods.

The examination of the dependence of selenophene and tellurophene depletion on laser flux was carried out with the entrance reactor window cleaned before each experiment. This helped to circumvent data irreproducibility caused by a gradual decay of laser power within the reactor, which was due to the build-up of selenium thin and tellurium films on the reactor window.

UV spectra of solid films, as deposited on quartz substrates, were recorded by using a Shimadzu UV 2100 spectrometer.

X-ray photoelectron spectra (XPS) were recorded using ESCA 3 Mk II (VG Scientific, UK) and ESCA 310 (Gammadata Scienta, Sweden) electron spectrometers, each equipped with an Al Kα (1486.6 eV) X-ray source and operated in the fixed-analyser transmission mode. XP spectra were recorded both as deposited samples and after mild argon-ion etching ($E = 5$ keV, $I = 20$ μA, 5 min) in order to remove the oxide layer grown on the surface of the sample during its transport to the spectrometer. Estimates of the deposit composition were made using the photoelectron peak areas and known sensitivity factors for each peak.

The morphology of the films was examined by scanning electron microscopy (a Tesla BS 350 ultra-high-vacuum instrument).

Selenophene (Aldrich, purity 97%) was a commercial sample. Tellurophene (purity better than 96%) was synthesized by a reported synthesis using bis(trimethylsilyl)-1,3-butadiyne and sodium telluride generated *in situ*.[11]

RESULTS AND DISCUSSION

The UV absorption spectrum of gaseous selenophene[12] shows an absorption band at 193 nm and continuous absorption between 210 and 260 nm, and that of gaseous tellurophene consists of three major bands at 196, 220 and 275 nm (Fig. 1). The absorptivities (in kPa^{-1} cm^{-1}) of C_4H_4Se and C_4H_4Te are, respectively, 0.73 and 0.43 (at 193 nm) and 1.7 and 0.13 (at 248 nm). They show that both compounds are good absorbers at both ArF and KrF laser irradiating wavelengths. The energy delivered by the photons of the ArF and KrF lasers corresponds respectively to *ca* 620 and 480 kJ $einstein^{-1}$. These energies are sufficient to cleave the two M–C (M = Se, Te) bonds, as the dissociation energies of the Se–C[13] and Te–C[14,15] bonds were estimated to be *ca* 250 kJ mol^{-1}. It appears that these energies are also enough to achieve cleavage of the two stronger M–C bonds in partially aromatic[16,17] tellurophene and selenophene.

Indeed, examination of the dependence of the depletion of both C_4H_4Se and C_4H_4Te compounds at both irradiating wavelengths on laser flux showed that the slopes of the depletion versus flux plots are close to unity and hence in line with a one-photon process.[10]

The ArF and KrF laser irradiation of gaseous selenophene and tellurophene results in the formation of 1-buten-3-yne and ethyne (as major products) and butadiyne (a very minor product) as

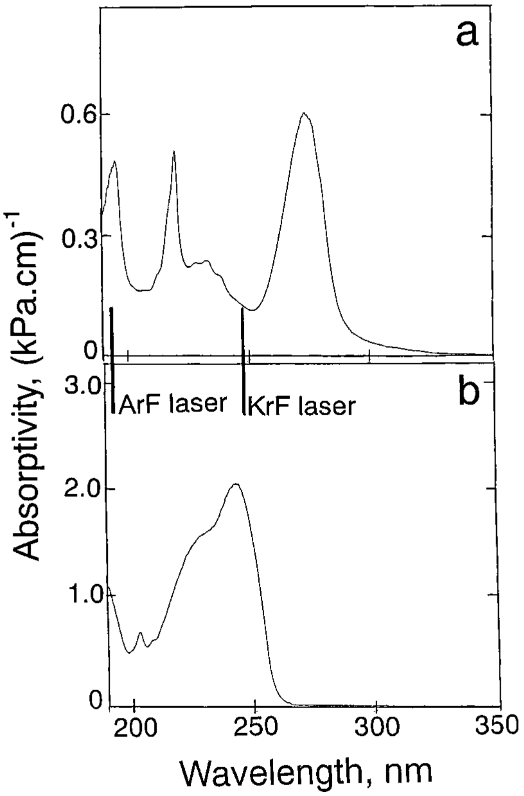
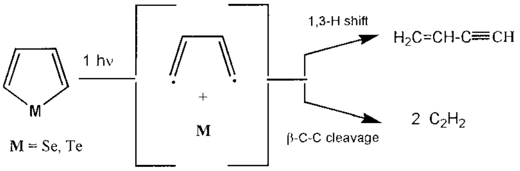


Figure 1 UV absorption spectrum of (a) tellurophene and (b) selenophene.

the exclusive volatile products. The formation of the same hydrocarbons shows that photolyses of both C_4H_4Se and C_4H_4Te compounds take place by the same mechanism[10] (Scheme 1). Further discussion on the role of the C_4H_4 intermediate and on the result of electronic excitation has been given in our preceding paper.[10]

Ethyne and 1-buten-3-yne practically do not absorb at 248 nm and their photolysis with 193 nm laser radiation is at least two orders of magnitude slower than that of tellurophene and selenophene. (J. Pola, unpublished results). These facts indicate that concurrent photolysis of the hydrocarbons is of negligible importance and that contamination of the deposited films by carbon-containing products must be insignificant.



Scheme 1

Irradiation of selenophene and tellurophene at 193 and 248 nm with fluxes of 5–60 mJ cm^2 resulted in the deposition of pink and dark films, respectively. The laser radiation was completely absorbed in the gaseous samples and the photolysis rate at both wavelength of each of the heterocyclopentadienes was virtually the same. The linear dependence of the photolytic depletion of selenophene and tellurophene on laser flux at both 193 and 248 nm, which gives support for a one-photon process, is illustrated in Fig. 2. The initial quantum yield of the 193 and 248 nm photolyses of selenophene was estimated to be 0.5–0.6, and those of tellurophene was *ca* 0.6. This small difference, along with a somewhat higher slope of the dependence for tellurophene (0.56 ± 0.5, Fig. 2b) compared with that for selenophene (0.45 ± 0.05, Fig. 2a), indicates a slightly more feasible cleavage of the Te–C bond.

Both films showed very good adhesion to the glass reactor surface and quartz.

XPS techniques did not reveal any difference in the film composition for films obtained with different flux. The films produced by the photolysis of selenophene are elemental selenium and contain some selenium dioxide and carbon in the topmost layers. This indicates that the selenium films were oxidized in air when transferred for analysis. The observed values of selenium 3*d* binding energies at 55.5 and 55.9 eV respectively are in accord with those of elemental selenium and selenium dioxide.[18] The smaller contribution of SeO_2 relative to that of selenium in the ion-sputtered sample compared with the one as-received is given in Fig. 3. The films obtained by the photolysis of tellurophene are elemental tellurium with some tellurium oxide in superficial layers. This is also consistent with surface oxidation of the films when they are exposed to air. The observed values of tellurium $3d_{5/2}$ binding energies at 573.2 eV correspond to elemental tellurium, while those at 576.2 and 578.5 eV reveal the presence of tellurium oxides[18] and are shifted due to differential static surface charging. Application of ion sputtering to removal of the most of the topmost oxide level and of differential charging is documented in Fig. 4. These films do not contain carbon in the topmost layers.

SEM analysis reveals that the morphology of the selenium and tellurium films differs. The selenium

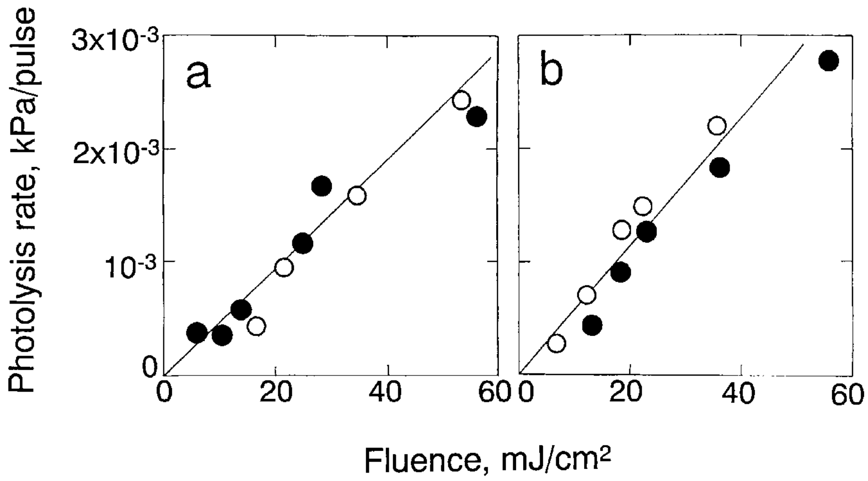


Figure 2 Depletion of (a) selenophene and (b) tellurophene versus laser flux: ●, ArF laser photolysis, ° KrF laser photolysis.

films have a structure of isolated round-shaped particles with diameters over 2 μm (Fig. 5a), whereas the tellurium films exhibit a unique agglomerate pattern of small particles (*ca* 0.3–0.5 μm) in which these particles are bonded into a continuous fluffy structure (Fig. 5b). This difference can be rationalized in terms of different deposition mechanisms. The formation of the specific microstructures was observed with both laser wavelengths. The higher pressure and hence a shorter photolysis zone in the selenophene (compared with the tellurophene) photolysis are in line with a higher concentration of the heteroatomic nuclei and hence more feasible formation of larger agglomerates in this process. We note that the observed ball-like morphology of selenium films was also observed with selenium films photodeposited from dimethylselenium (see J. Pola, Z. Bastl, J. Šubrt, A. Ouchi, unpublished results). and with selenium films produced upon evaporation/

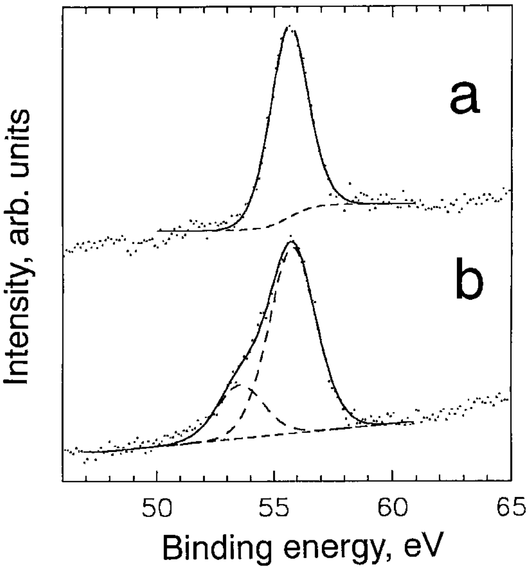


Figure 3 Photoelectron spectrum of Se 3*d* electrons in films from selenophene (a) after and (b) before ion sputtering.

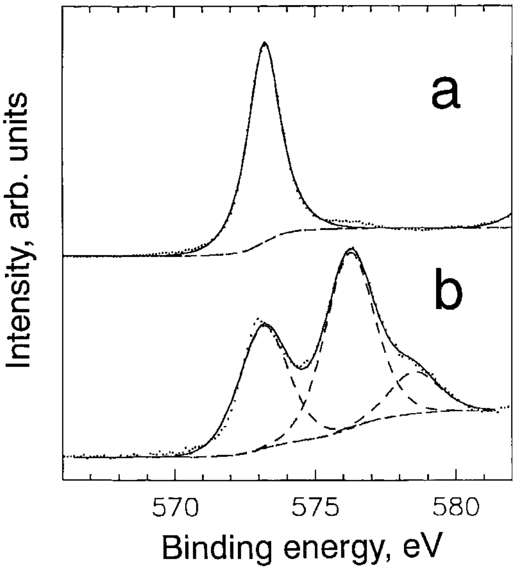


Figure 4 Photoelectron spectrum of Te 3*d*5/2 electrons of films from tellurophene (a) after and (b) before ion sputtering.

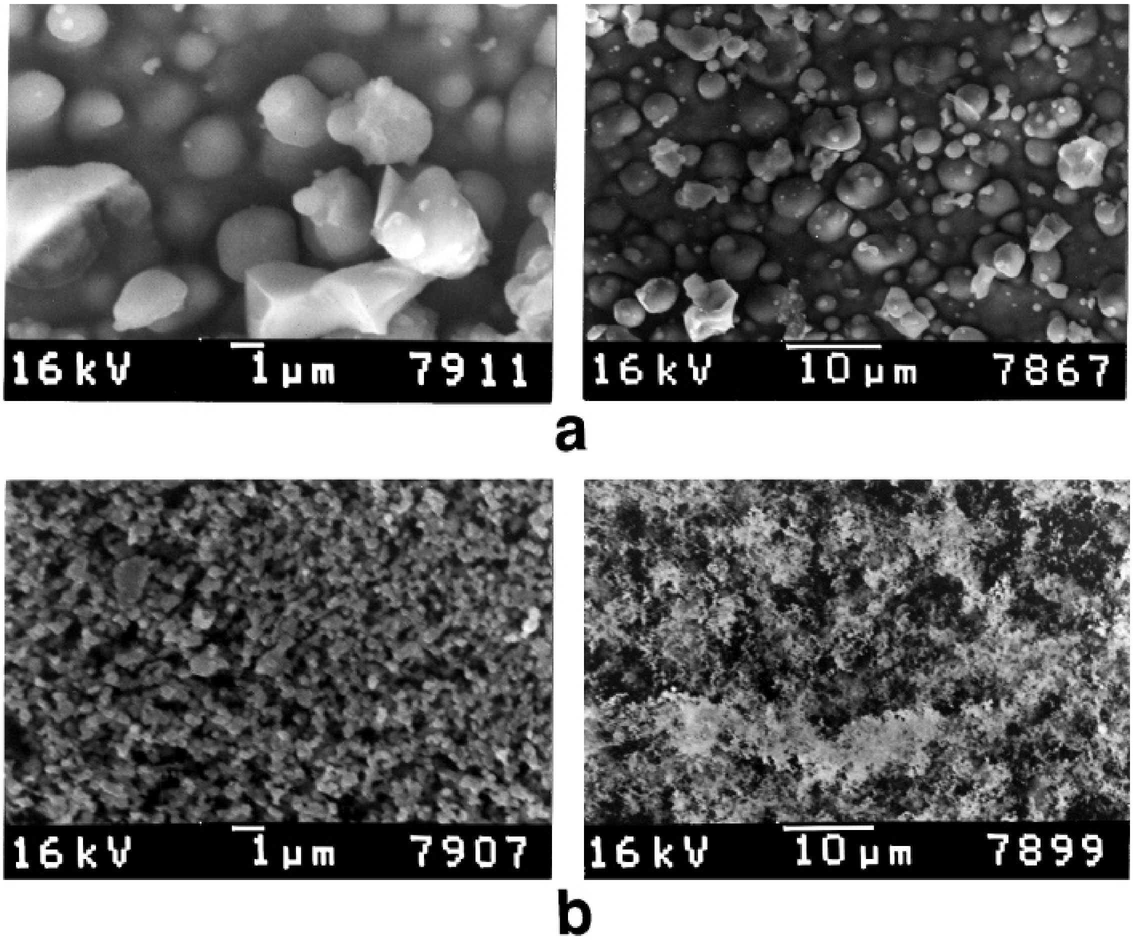


Figure 5 Typical SEM image of (a) selenium and (b) tellurium films.

deposition of selenium.[19] We also remark that the fluffy-particle morphology of tellurium films has not been previously reported.

UV/Vis absorption spectra of the selenium and tellurium films have very similar patterns in the region of 190–700 nm (Fig. 6). They show a broad maximum at 280 nm (Se) and 300 nm (Te) and a decreasing absorbance towards higher wavelengths. The observed spectrum of the selenium films is consistent with that of amorphous selenium, which is known[20] to exhibit two strong maxima, at 140 and 287 nm. The observed spectrum of tellurium differs from those of thin granular tellurium films[21,22] and of thick tellurium layers.[23] These possess absorption maxima at 600 nm assigned to inter-zone transitions[24] and which become lost due to quantum dimensional effects when the granular films become thinner than 9 nm. We can speculate that the absence of the 600 nm band in the spectrum of the tellurium films obtained in this work is associated with different morphologies, since the granular films[21,22] consisted of nanometre-sized separate islands.

Conclusion

ArF and KrF laser photolysis of gaseous selenophene and tellurophene affords CVD of selenium and tellurium films which are not contaminated by carbon from hydrocarbon photolytic by-products. The photolysis of both heterocyclopentadienes is of interest for deposition of selenium- and tellurium-containing films, which find use as II–VI semiconductor films (e.g. Ref. 25.) or are important optical data storage applications (e.g. Ref. 26.).

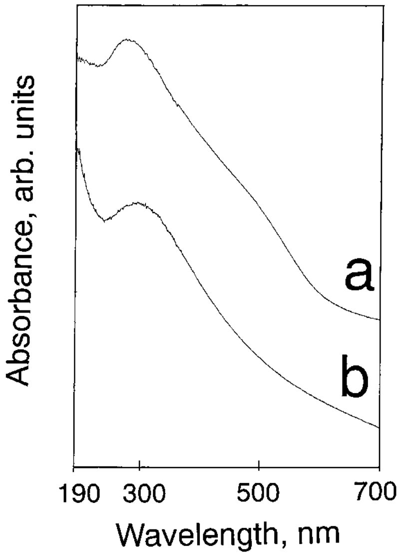


Figure 6 Typical UV/Vis absorption spectrum of (a) selenium and (b) tellurium films.

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