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Deposition of nanostructured Te and Te/C particles by excimer laser-induced photolysis of organotelluriums in the liquid phase

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Excimer laser induced photolysis of dialkyltellurides R_2Te ($R = C_2H_5$, n-C_5H_{11}) and tellurophene in *n*-hexane affords nanostructured Te and Te/C particles the surface of which is oxidized in the atmosphere and whose C content depends on the structure of the organotellurium precursor.

Introduction

The production of fine metal particles has recently received much attention due to their unique features such as large surface areas, unusual adsorptive properties and surface defects which make them suitable for many applications, especially in catalysis and microelectronics. Relatively large tellurium particles have been traditionally used to improve working properties of steel and lead, while smaller (sub-micron-size) particles are expected to find application in thermoelectric and optoelectric devices. Ultrafine tellurium particles have up to now been produced by homogeneous reduction of Te(IV) bromide with alkalides and electrides in aprotic solvents,[1,2] electroless reduction by Ti(III) complexes in the presence of stabilizing agents like polyvinyl alcohol,[3] electro-reduction of $HTeO^{2+}$ in aqueous media,[4] electro-oxidation of tellurides in cationic surfactant–aqueous sodium hydroxide suspensions,[5] electron beam-induced decomposition of tellurium azide,[6] and γ-irradiation of tellurium(IV) oxide in concentrated hydrochloric acid containing sodium dodecyl sulfate surfactant.[7] They can be also prepared by laser ablation of tellurium targets[8] and by a high-pressure Hg lamp photolysis of R_2Te (R = methyl, ethyl) compounds.[9] UV irradiation of metal alkyls is a convenient method for production of metal atoms from gaseous precursors.[10,11] Volatile dialkyl tellurides show[9] several absorption bands between 190 and 250 nm and they were Hg lamp,[12,13] or laser,[14–17] photolysed in the gas phase to produce Te atoms[15–17] for achieving laser-induced surface chemical epitaxy[18–20] or growth of thin films of II–VI compounds.[21,22]

Despite the considerable body of data on organotellurium photochemistry in the gas phase, photochemical formation of tellurium from organotelluriums in the liquid phase has been very little examined. Tellurium mirrors were unintentionally produced and not characterized in an Hg lamp-initiated study on the photo-rearrangement of 2-phenyltellurophene[23] and in EPR spectral study on the formation of organyl radicals from diorganyl tellurides.[24]

In an earlier paper we reported that excimer laser-induced solution photolysis of organogermanes can be used for deposition of films composed of submicrometer-sized particles of germanium.[25] Here we show that the technique of excimer laser-induced photochemistry is suitable for production of Te and Te/C particles from solutions in *n*-hexane of tellurophene and R_2Te (R = ethyl, *n*-pentyl) compounds. We have discovered that the deposition of Te particles is accompanied by degradation of hydrocarbon products into carbon, and that the importance of this side-reaction is dependent on the structure of the organotellurium compound.

Experimental

Samples of organotelluriums (diethyl tellurium, di-*n*-pentyl tellurium and tellurophene), 5×10^{-4} molar, 10^{-3} molar and 1.5×10^{-2} molar in *n*-hexane (spectroscopic grade, Cica-Merck) were stirred by a magnetic bar in a 4 ml ($4 \times 1 \times 1$ cm, optical path 1 cm) quartz cell under argon and irradiated with an excimer laser with a repetition frequency of 10 Hz for periods of 3–5 min which was sufficient for a complete decomposition of the organotelluriums. Three different excimer lasers were used, an ArF (Lambda Physik CPX 200) laser emitting at 193 nm with an energy fluence of 50 mJ cm^{-2}, a KrF (EMG 201 MSC Lambda Physik) laser operating at 248 nm with an energy fluence of 150 mJ cm^{-2}, and a XeCl (EMG 102 MSC Lambda Physik) laser lasing at 308 nm with an energy fluence of 30 mJ cm^{-2}. The effective radiation area was in each case 0.25 cm^2.

The progress of the photolytic decomposition of the organotelluriums was monitored *via* the depletion of the absorption bands centered at 236 nm (R_2Te) or 279 nm (C_4H_4Te). After the irradiation, black particles formed during the photolysis were centrifuged from the solution, washed with *n*-hexane and again centrifuged. They formed thick films when their *n*-hexane suspensions were dropped on a metal sheet heated on a hot plate (temperature *ca.* 100 °C). These films were analysed by X-ray photoelectron spectroscopy (XPS) and by transmission electron microscopy (TEM). The centrifuged solutions freed of the black particles were analysed by gas chromatography [Gasukuro Kogyo model 370 chromatographs, 60 m Neutra Bond-T capillary column and 2 m Unipak SUS column (both GL Sciences, Inc.)] to identify organic products by comparing their retention times with those of authentic samples. Brown solid particles, developed after 1–2 hours in the centrifuged solutions after photolysis of tellurophene, were analysed on a Shimadzu FTIR 4000 spectrometer.

XPS analyses were performed with a Perkin Elmer PHI 5600 system using monochromated Al-Kα X-ray radiation. The spectrometer was tuned to a precision of Au $4f_{7/2}$ = 84.0 eV, Ag $4d_{5/2}$ = 368.3 eV and Cu $2p_{3/2}$ = 932.7 eV. Before all measurements, the line position C 1s = 284.5 eV of highly oriented pyrolytic graphite was used as a bonding energy reference. The data are presented after inelastic background subtraction and peak separation using Gaussian curve fits. Quantification of the surface concentrations of the elements was accomplished by correcting the photoelectron peak areas for their cross sections.[26] Samples were sputtered by Ar ions with energy of 1 keV for 5 s and 3 min.

Bright field TEM images and electron diffractographs were

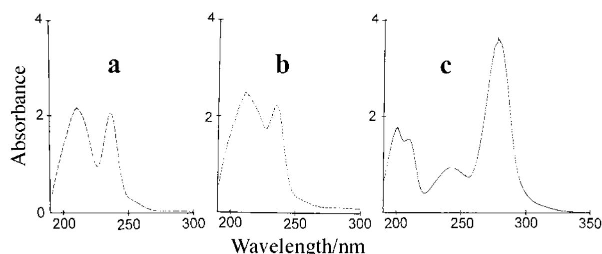


Fig. 1 UV absorption spectra of 5×10^{-4} molar solutions in *n*-hexane of diethyltelluride (a), di-*n*-pentyl telluride (b) and tellurophene (c).

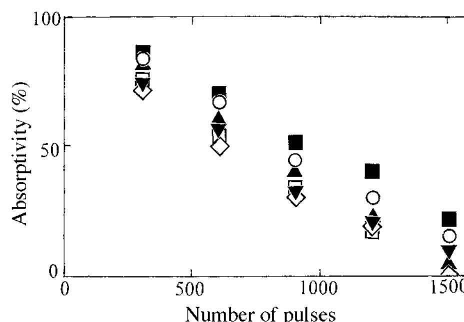


Fig. 2 Depletion of the 236 nm (R_2Te) and 279 nm (C_4H_4Te) absorption bands as dependent on the number of laser pulses in irradiation of 5×10^{-4} molar solutions of the organotelluriums in *n*-hexane. ArF laser ($f=50$ mJ cm^{-2}) irradiation of diethyl telluride (○) and tellurophene (■); KrF laser ($f=50$ mJ cm^{-2}) irradiation of di-*n*-pentyl telluride (□), diethyl telluride (◇) and tellurophene (▼); XeCl laser ($f=30$ mJ cm^{-2}) irradiation of tellurophene (▲).

obtained using a JEOL 2000 FX microscope. The operating voltage was 200 kV. The samples were removed from Si substrates and ground using an agate mortar, and held with a copper grid for TEM observations.

UV spectra of organotelluriums in *n*-hexane were recorded on a Shimadzu UV-2100 spectrometer.

The dialkyl telluriums R_2Te (R = ethyl and *n*-pentyl)[27] and tellurophene[28] were prepared following reported procedures and obtained by distillation as fractions with bp 85 °C/120 Torr (diethyl tellurium), 114 °C/8 Torr (di-*n*-pentyl tellurium) and at 88 °C/85 Torr (tellurophene). Their purity was checked by gas chromatography (a Gasukuro Kogyo model 370 chromatograph, 60 m Neutra Bond-T capillary column) and by ^{1}H and ^{13}C NMR spectroscopy ($CDCl_3$ solutions, Bruker AC-200 spectrometer).

Results and discussion

Diethyl telluride and di-*n*-pentyl telluride show strong UV absorption at the ArF and KrF laser emissions, and tellurophene shows strong absorption bands at the ArF, KrF and XeCl laser emissions (Fig. 1, Table 1). Laser irradiation of solutions of organotelluriums in *n*-hexane for several minutes resulted in initial darkening of the solutions and later formation of black particles. Very small bubbles observed to arise from the irradiated spot behind the front cell wall revealed formation of gaseous products expelled from the solutions. We therefore presume that the photolytic decomposition takes place mostly behind the quartz–liquid interface.

The photolytic progress for the individual organotelluriums upon irradiating 5×10^{-2} molar *n*-hexane solutions is not strongly affected by their structure (Fig. 2). Although the slowest photolytic progress was observed with the ArF laser irradiation of tellurophene and the fastest with the KrF laser irradiation of R_2Te compounds, the depletion of all the organotelluriums with the different lasers (ArF, KrF and XeCl) are very similar. Laser radiation was in all cases completely absorbed in the solutions. Thus, the observed small differences in the organotelluriums depletion should not be related to different absorptivities of the organotelluriums at each laser wavelength (Table 1), but rather to differences in the deposited energy fluence. We surmise that the absence of an enhanced depletion with the more intense KrF laser irradiations may be due to a combination of photolytic and thermal decomposition and/or due to the development of Te particles which can obstruct photolysis.

Table 1 UV absorption maxima and molar absorptivities of organotelluriums

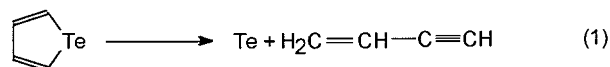
Organotellurium	λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})	$\varepsilon_{193\ nm}$	$\varepsilon_{248\ nm}$	$\varepsilon_{308\ nm}$
$(C_2H_5)_2Te$	210(4500), 236(4300)	1200	800	—
$(n\text{-}C_5H_{11})_2Te$	211(4900), 236(4400)	1800	750	—
C_4H_4Te	201(4270), 210(3700), 242(2260), 279(8700)	2450	2050	550

Photolytic steps

The energy delivered by the photons of the ArF, KrF and XeCl lasers corresponds respectively to *ca.* 620, 480 and 390 kJ einstein^{-1}, and is much in excess of the energy needed for the cleavage of Te–C (*ca.* 280 kJ mol^{-1}, ref. 29), C–C (*ca.* 340 kJ mol^{-1}) and C–H (*ca.* 400 kJ mol^{-1}) bonds. All types of cleavage are therefore possible, but we judge that the photolysis is most likely initiated by homolysis of the weakest Te–C bond.

Photolysis and thermolysis of R_2Te compounds can, in principle, occur[24,29] *via* a four-centred transition state involving β-elimination ($R_2Te \rightarrow$ alkene + RTeH) to yield alkenes, or *via* homolysis of Te–C bonds ($R_2Te \rightarrow R^{\cdot} + RTe^{\cdot}$, $RTe^{\cdot} \rightarrow R^{\cdot} + Te$) to yield reactive R radicals which can undergo a number of consecutive reactions such as cleavage, self-combination, disproportionation and H-abstraction. Although products of these reactions arising from diethyl telluride are gases and escaped from the solution, some less volatile products formed from di-*n*-pentyl telluride were detected by gas chromatography; *n*-decane, *n*-heptane, a C_6 hydrocarbon and pentane, their relative amounts being $n\text{-}C_{10}H_{22} \gg C_5H_{12} \approx C_7H_{16} \approx C_6$ hydrocarbon.

Photolysis of tellurophene has not yet been studied, but we can judge that Te atoms are produced by a cleavage affording but-1-en-3-yne [eqn. (1)], since weak and slowly depleting absorption bands of this compound at 219 and 227 nm (ref. 30) were observed during all the photolytic runs.



(We note that this reaction has an analogy in the reported photolysis of 2-phenyltellurophene[23] into 4-phenylbut-1-en-3-yne, and in our observation of the gas-phase tellurophene photolysis into Te, but-1-en-3-yne and ethyne.[31]) These absorption bands disappear completely after 1–2 hours after which time centrifuged *n*-hexane solutions lose their yellow colour and deposit brown particles. This phenomenon is in keeping with but-1-en-3-yne polymerization, since the IR spectrum of these particles [wavenumber/cm^{-1}, (normalised absorptivity): 3264 (66), 3040 (45), 2976 (66), 1620 (55), 1568 (60), 1388 (10), 1306 (15), 1056 (30), 1018 (30) and 640 (100)] is consistent with a polymer retaining a large fraction of C=C and C≡C bonds.

Composition of the deposited particles

XPS analysis of the black particles (coatings produced from the *n*-hexane suspensions, Table 2) revealed that *ca.* 5 nm thick layers contain tellurium, carbon and oxygen. The observed

Table 2 XPS analysis of black particles[a] obtained at different irradiation conditions

	Irradiation parameters		Surface composition[b] (at.%)			Surface composition[c] (at.%)			Binding energy[c]/eV		
Organotellurium	Laser	Fluence/mJ cm^{-2}	Te	C	O	Te	C	O	Te 3d$_{5/2}$	C 1s	O 1s
$(C_2H_5)_2Te$	ArF	50	44	24	32	67	8	25	573.1 576.8	284.8	530.5
	KrF	150	24	21	35	64	6	30	572.6 575.5	284.2	529.8
$(n\text{-}C_5H_{11})_2Te$	ArF	50	38	35	27	67	18	15	573.1 575.9	284.8	530.3
	KrF	150	33	41	25	59	21	20	573.1 576.2	284.8	530.5
C_4H_4Te	ArF	50	34	46	20	63	34	3	573.3	284.6	530.8
	KrF	150	26	56	18	39	56	5	573.2	284.5	531.0
	XeCl	30	29	52	19	54	42	4	573.0	284.2	531.6

[a]Produced from 1.4×10^{-2} molar solutions of organotelluriums in *n*-hexane after 10 min laser irradiation. [b]After 5 s sputtering. [c]After 2 min sputtering.

values of C 1s binding energies (284.2–284.8 eV), O 1s binding energies (529.9–531.6 eV) and Te 3d$_{5/2}$ binding energies (572.6–573.3 and 575.5–576.9 eV) are in good accord with those of elemental carbon, elemental tellurium and tellurium dioxide.[26]

The relative amounts of these elements, as well as the proportions of Te and TeO_2 are not much affected by the laser wavelength, but depend on the precursor and are altered after Ar-ion sputtering (Table 2, Fig. 3 and 4). Although the removal of the surface impurities was incomplete due to the roughness of the surface, the decrease of the content of oxygen and carbon upon ion sputtering reveals that both elements were contained in the topmost layers.

The 3d$_{5/2}$ core level spectra of the surface of the particles deposited from the R_2Te compounds using the ArF and KrF lasers (Fig. 3) differ from those of the particles deposited from tellurophene by the ArF, KrF and XeCl lasers (Fig. 4). The former are composed of TeO_2 as a major and Te as a minor constituent, and prolonged Ar-ion sputtering changes the ratio of the constituents in favour of Te (Fig. 3). 3d$_{5/2}$ Core level spectra of the coatings deposited from tellurophene show Te as a major and TeO_2 as a minor component, and prolonged Ar-ion sputtering completely removed the minor TeO_2 phase (Fig. 4). These features reveal that (i) TeO_2 is contained in the topmost layers and that (ii) Te is more easily oxidized when produced from the R_2Te compounds. The origin of this different reactivity of Te particles, as yet, remains unclear; we may only hypothesize that it is related to the concomitant occurrence of elemental carbon.

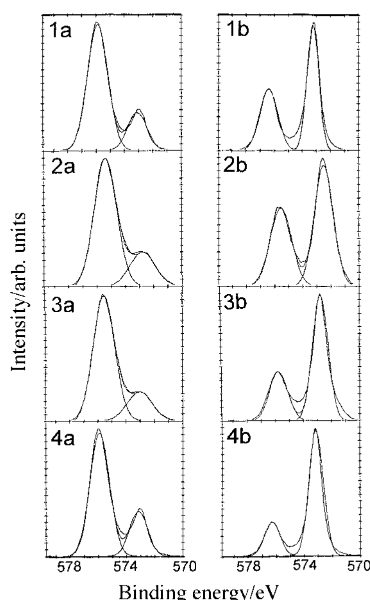


Fig. 3 Te 3d$_{5/2}$ core level spectra of particles obtained from diethyl telluride by using ArF laser (1) and KrF laser (2), and of particles obtained from di-*n*-pentyltelluride by using KrF laser (3) and ArF laser (4) (a and b relate to 5 s and 2 min Ar ion sputtering, respectively).

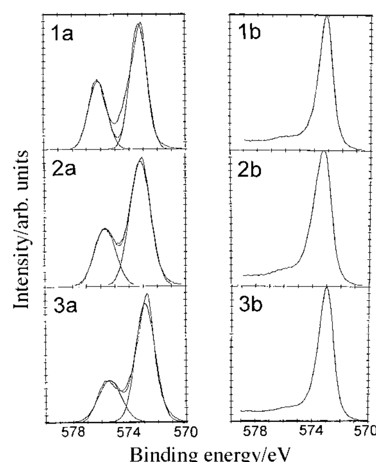


Fig. 4 Te 3d$_{5/2}$ core level spectra of particles obtained from tellurophene by using ArF laser (1), KrF laser (2) and XeCl laser (3) (a and b relate to 5 s and 2 min Ar ion sputtering, respectively).

The content of the elemental carbon is essentially unaffected by laser wavelength and fluence, but is strongly dependent on the structure of the organotellurium compound. The carbon content is substantially reduced after 5 min Ar-ion sputtering only in the samples from $(C_2H_5)_2Te$, and only little decreased in the samples from $(n\text{-}C_5H_{11})_2Te$ and tellurophene (Table 2). This indicates that carbon is mostly a contaminant in the former and a photolytic product in the latter. We assume that UV laser photolytic formation of carbon, earlier observed for some aromatic compounds,[32,33] is a consequence of degradation of hydrocarbon intermediates and/or products. This degradation will be more feasible in photolysis of $(n\text{-}C_5H_{11})_2Te$ and tellurophene, wherein the presumed unsaturated C_5 fragments and the identified but-1-en-3-yne (or its polymer) are stronger UV absorbers. Their photolytic degradation should therefore be easier than that of C_2 fragments formed in the photolysis of $(C_2H_5)_2Te$. (Solvent degradation can be ruled out on the basis of the absence of carbon formation in the ArF, KrF and XeCl laser photolysis of neat *n*-hexane).

TEM examination of the coatings produced from 5×10^{-4}, 10^{-3} and 1.5×10^{-2} molar solutions revealed that they are polycrystalline and that they are composed of particles <100 nm. TEM images of the coatings obtained from tellurophene by using KrF laser excitation and of the dialkyltellurides obtained by using a ArF laser are given as illustrative examples (Fig. 5).

In summary, ArF, KrF and XeCl laser photolysis of tellurophene and R_2Te ($R = C_2H_5$, $n\text{-}C_5H_{11}$) compounds is controlled by cleavage of the Te–C bond to produce elemental tellurium, and is accompanied by degradation of hydrocarbon products into carbon. The importance of the latter increases

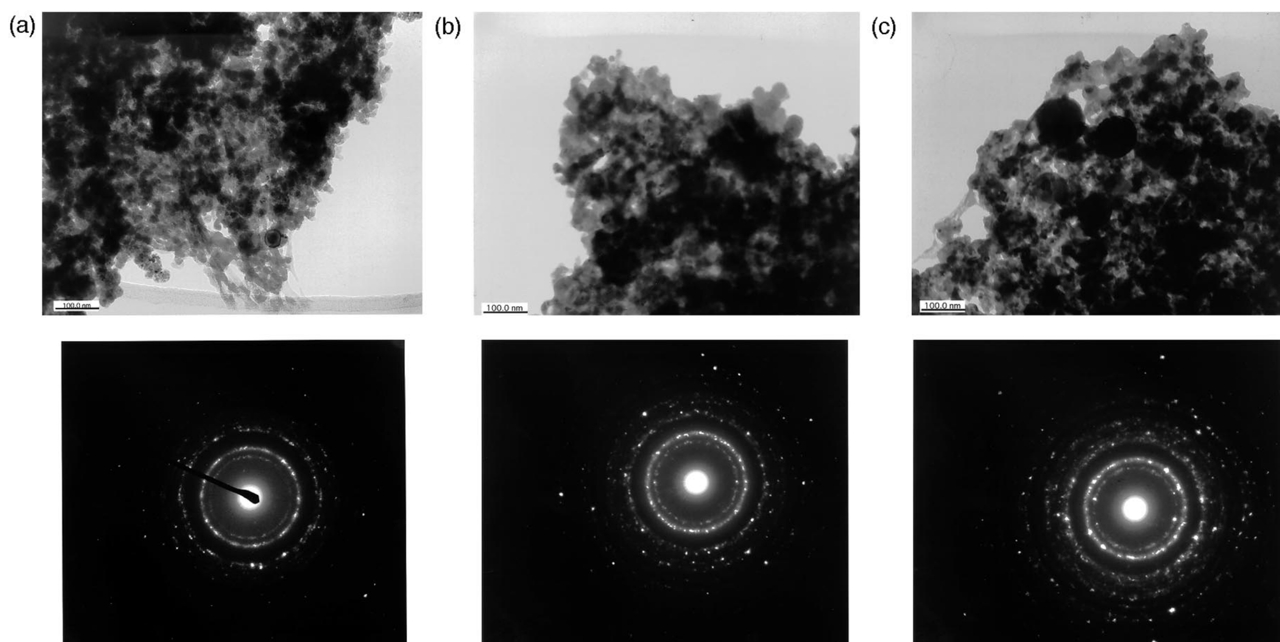


Fig. 5 TEM images and corresponding diffraction patterns of the coatings obtained from KrF laser irradiation of tellurophene (a) and ArF laser irradiation of diethyltelluride (b) and di-*n*-pentyltelluride (c).

in the series $(C_2H_5)_2Te < (n\text{-}C_5H_{11})_2Te < C_4H_4Te$. The UV laser photolysis of diethyl telluride is demonstrated as a suitable technique for liquid-phase deposition of submicrometer particles of tellurium, and the UV laser photolysis of tellurophene and di-*n*-pentyl telluride is shown as a suitable technique for liquid-phase deposition of submicrometer particles of tellurium and carbon.

Acknowledgements

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