Pulsed-Laser Deposition of Metal Acetyl Acetonates for Sensor Devices

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ABSTRACT: Thin layers of tin acetyl acetonate (SnAcAc) were deposited by the laser ablation deposition (LAD) method onto potassium bromide tablets. FTIR and X-ray photoelectronspectroscopy (XPS) spectra of these layers were investigated to describe changes in chemical composition during the deposition and following a thermal activation process. The main interest was focused on the formation of systems containing conjugated double bonds, tin dioxide (SnO_2), tin suboxides (SnO_x; $x < 2$), and salts (especially carboxylates). These phases play an important role in the use of LAD-deposited acetyl acetonates as active layers of chemical sensors. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1614–1622, 1999

Key words: laser deposition; acetyl acetonates; FTIR spectra; XPS spectra; chemical sensors

INTRODUCTION

At the end of the 1980s, the first information was published[1] on the possibility of laser depositing some organic substances. When employing the laser ablation deposition (LAD) method, excimer laser pulses are aimed at a target pressed from the original substance (without using adhesives). If the energy density of laser radiation and the composition and pressure of the surrounding atmosphere are suitable, a plasma plume is formed above the exposed target area, extending to a distance of several tens of millimeters. These ablation products are deposited on a closely localized substrate and form a thin layer of deposited substance. The LAD technology can be used for the deposition of both organic and inorganic substances.[2] It has several advantages in comparison with conventional deposition methods [thick-layer technology, sputtering, radiofrequency (RF) sputtering]. The basic advantages of employing LAD technology in the deposition of active layers for sensor devices are (1) LAD technology needs no solvents (typical for thick layer technology); (2) it permits precise control of deposition of multilayer structures *in situ* in one technological step (impossible in RF sputtering); (3) in our experiments, the LAD-deposited SnAcAc sensors achieved significantly higher sensitivities to hydrogen (on an average, five times) and carbon monoxide (on an average, four times) in comparison with analogical thick-layer technology sensor; (4) the chemical sensors with LAD-deposited active layers also exhibit good stability and reproducibility of their properties after thermal activation.
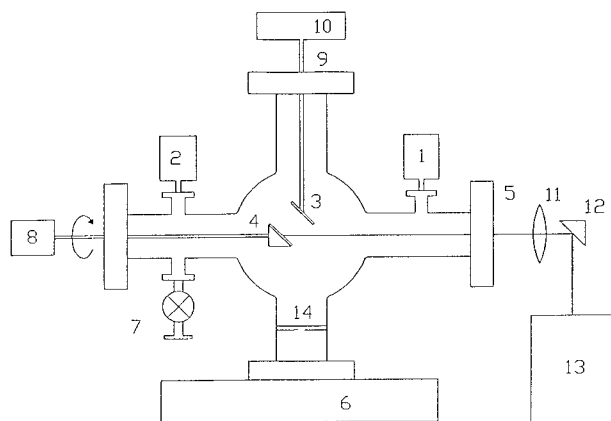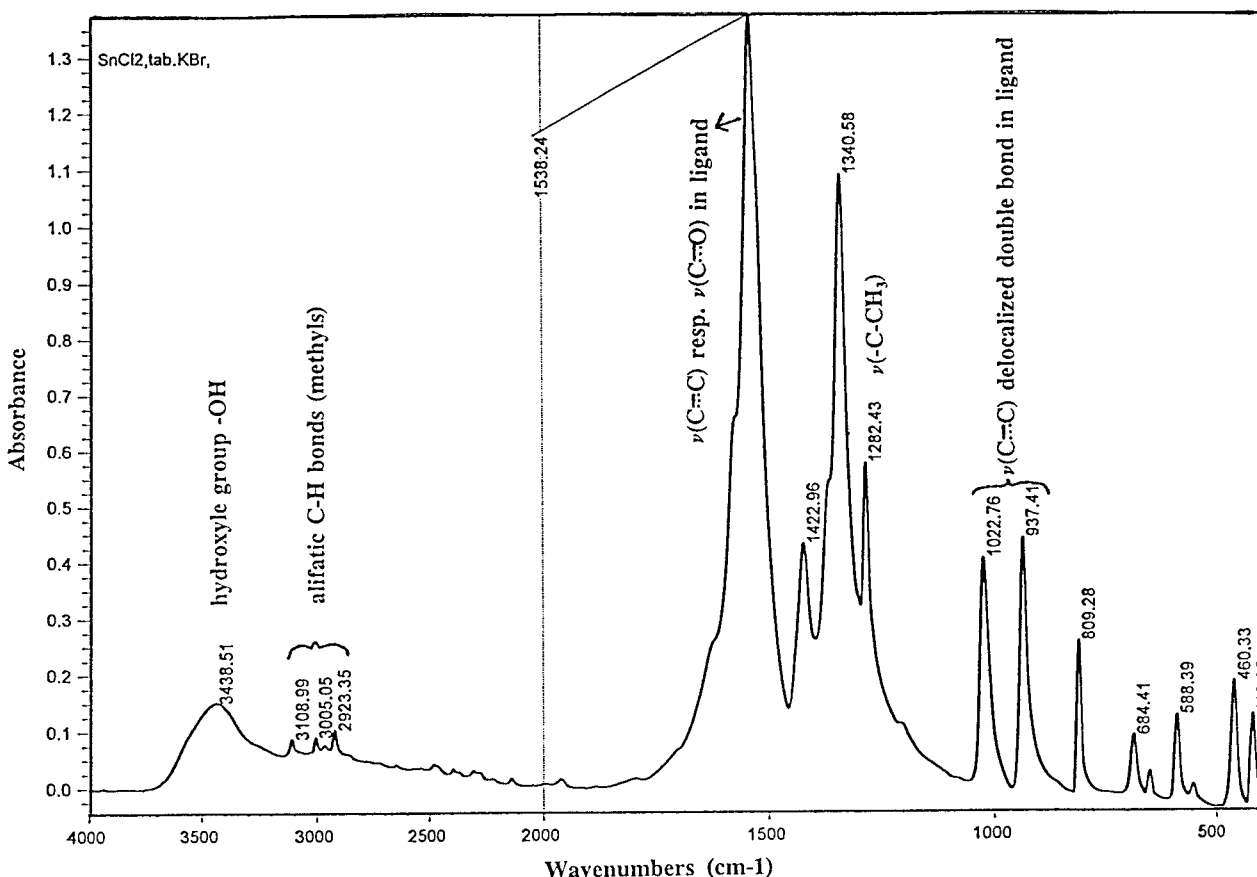
Figure 1 The technological set-up for LAD (laser ablation deposition) method. (1) Penning gauge; (2) Pirani gauge; (3) substrate holder; (4) target holder; (5) input quartz window; (6) vacuum stand; (7) inert gas outlet; (8) rotary equipment; (9) heat input; (10) heating unit and thermometer; (11) quartz lens; (12) quartz prism; (13) excimer KrF laser; (14) filters.

Metallic complexes of organic ligands such as acetyl acetonates and phthalocyanines, together with some polymers containing polarizable bonds (polyethers, polyurethanes, polypyrroles, polythiophenes), are promising materials for active layers of chemical gas sensors.[3,4] Acetyl acetonates were chosen because they yielded promising results, such as RF-sputtered sensor layers.

The layers as-deposited from acetyl acetonate targets were not electrically conductive. Because of this fact, the as-deposited layers must be subjected to thermal activation. After thermal treatment, the layers exhibit semiconductive behavior and are sensitive to a reducing atmosphere. This contribution presents FTIR spectra of both as-deposited and thermally activated acetyl acetonate layers with respect to the formation of the following phases: (a) metallic oxides (SnO_2, In_2O_3), (b) organic systems with conjugated double bonds, (c) carboxylates of the mentioned metals (—COO^- groups bonded on polymeric chain are typical products of acetyl acetonate degradation). Although (a) and (b) phases are desirable for sensing, the presence of nonconductive and nonpolarizable carboxylates leads to the degradation of sensing properties.

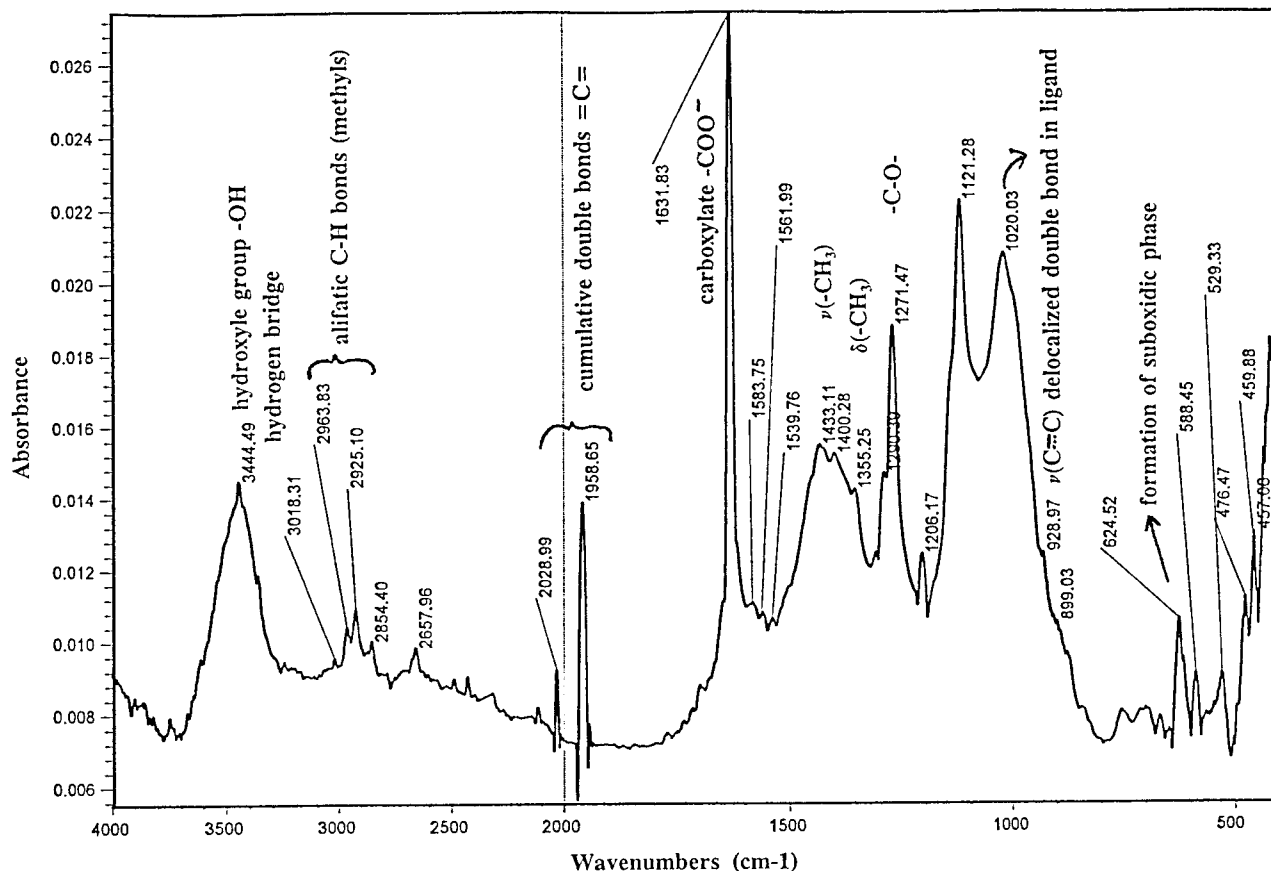**Figure 2** The FTIR spectrum of pure SnAcAc target material.
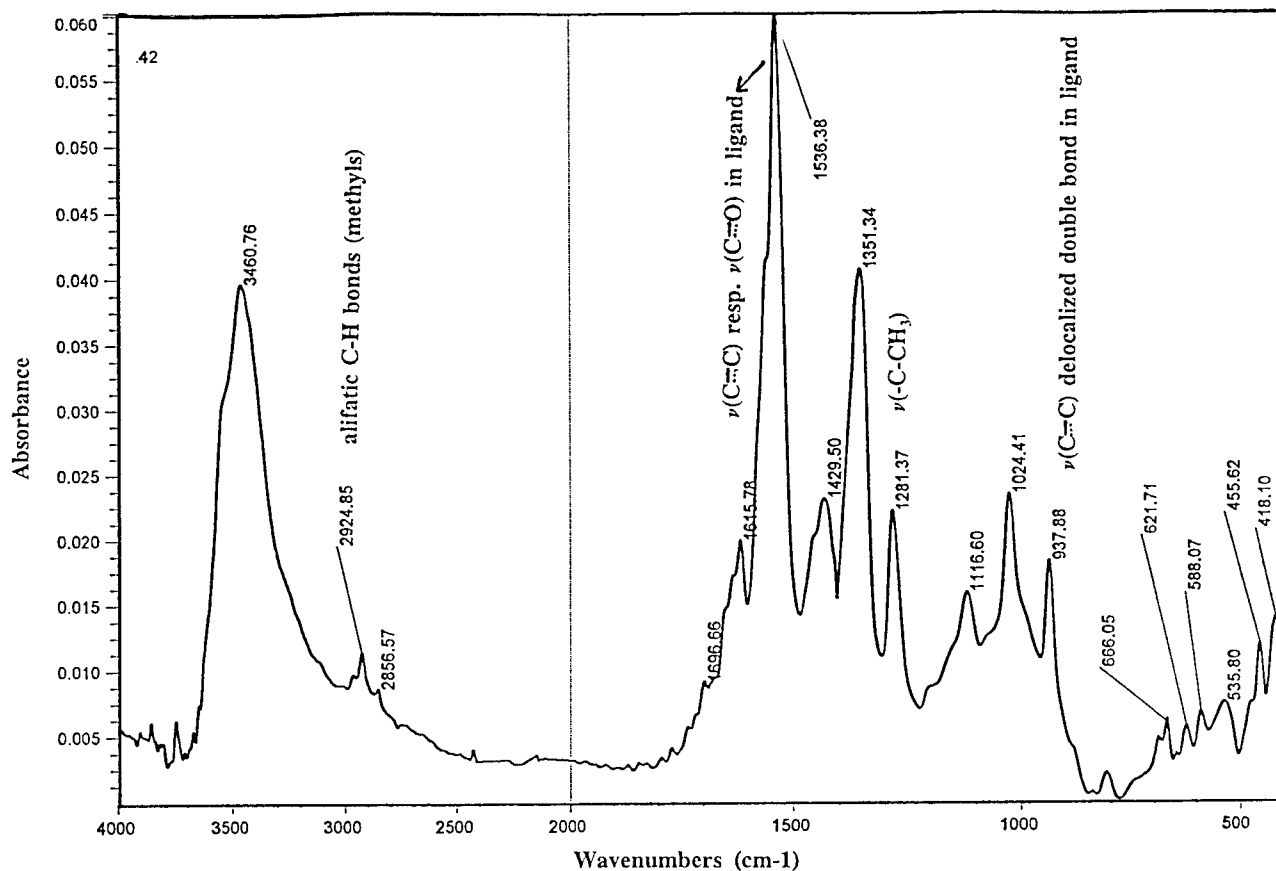
Figure 3 The FTIR spectrum of a layer as-deposited from SnAcAc target (energy density of laser radiation $E_l = 0.15$ J cm^{-2}).

EXPERIMENTAL

The basic technological set-up for LAD technology is shown in Figure 1. An excimer KrF laser generates radiation at a wavelength of 248 nm, energy of up to 190 mJ/pulse. The full width at half maximum (FWHM) is about 15 ns and the repetition rate of laser pulses is 5 Hz. After focusing (11) and passing through an aperture, the laser radiation passes through a fused silica window (5) into the working chamber and is incident on a target (4) prepared from the source substance. Rotating the target suppresses formation of a deep hole, which appears as a result of repeated exposure of a single spot. The target substrate (3) distance is 35 mm. The vacuum system (6) permits the evacuation of the deposition chamber to a residual pressure of 10^{-4} Pa and the subsequent filling with the working atmosphere at a pressure ranging from 1 to 100 Pa.

The single-component targets of acetyl acetonate SnAcAc and oxide SnO$_2$ (Aldrich Chemi-

cals, Milwaukee, WI, USA) were pressed from powder material under a pressure of 85 MPa; the volume contraction was 1/5–1/3. The deposition from the target to potassium bromide substrates lasted for 5 min in all cases. A typical thickness of the deposited layers was 100 nm. Although an inert nitrogen atmosphere was used during the deposition of acetyl acetonate, the oxide was deposited in oxygen to prevent its decomposition. The pressure of working gas was 5 Pa in most cases. The only exception occurred during the investigation of the influence of working gas pressure on the properties of deposited layers. This experiment was carried out with SnAcAc; the pressure of nitrogen changed in steps 0.1, 1, 5, 10, 30, and 100 Pa, and the energy density of laser radiation was constant at $E_l = 0.3$ J cm^{-2}. In all other cases, the depositions were carried out under a pressure of 5 Pa with the following energy densities (E_l) of laser radiation: 0.15, 0.3, 0.6, 0.9, 1.2, and 1.5 J cm^{-2}. The thermal activation of as-deposited acetyl acetonate layers was carried out at 430°C

Figure 4 The spectrum of the same layer as in the previous case after thermal activation (9 h at 430°C in 5000 ppm).

for 9 h in a synthetic air atmosphere (80% N_2, 20% O_2, $C_nH_m < 0.1$ ppm) containing 5000 ppm of hydrogen.

RESULTS AND DISCUSSION

FTIR Spectroscopy

The set of Figures 2–5 compares the following FTIR spectra: Figure 2, spectrum of the pure SnAcAc target material; Figure 3, spectrum of a layer as-deposited from SnAcAc target ($E_l = 0.15$ J cm^{-2}); Figure 4, spectrum of the same layer as in the previous case after thermal activation; Figure 5, spectrum of the pure SnO_2.

In the spectrum of the pure SnAcAc (Fig. 2), characteristic absorption peaks appear at 1538 (νC$\cdots$C and νC$\cdots$O delocalized double bond in ligand) and 1282 cm^{-1} [ν(C—CH$_3$)]. A significant double peak at 1023 and 937 cm^{-1} also corresponds to ν(C$\cdots$C) and ν(C$\cdots$O) and demonstrates the presence of acetyl acetonate phase in

all these spectra. On the other hand, the absence of a noticeable peak in the vicinity of 658 cm^{-1} proves that the oxidic phase is not present.

The strongest peak of acetyl acetonate at 1536 cm^{-1} persists also in the spectrum of the as-deposited layer (Fig. 3); one at 1282 is also present, and even the abovementioned double peak can be identified. It retains only the position of both maxima, but not a characteristic shape. A strong peak at 1351 cm^{-1} probably corresponds to δ(—CH$_3$). No peaks corresponding to oxidic phase are noticeable.

The thermal activation of the deposited layer is accompanied by more significant changes in its chemical composition (Fig. 4). The new maxima at 2003 and 1958 cm^{-1} appear because of the presence of cumulated double bonds between carbon atoms. The strongest peak at 1631 cm^{-1} corresponds to carboxylate —COO$^-$ groups, which are bonded on the carbon chain. The maximum at 1538 cm^{-1}, typical for delocalized double bonds in the ligand cycle, disappears completely. In con-
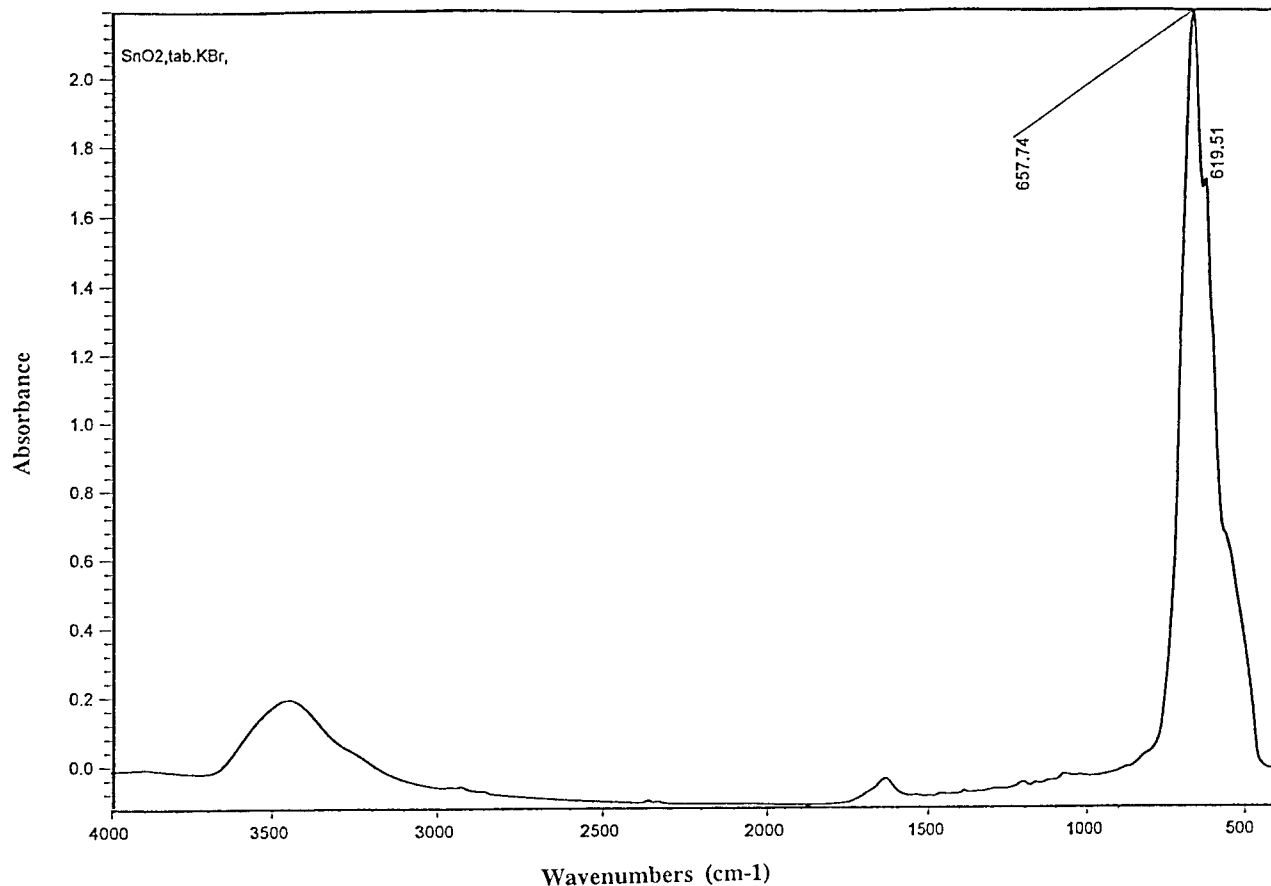
Figure 5   The FTIR spectrum of pure SnO_2.

trast, the new peak at 1271 cm^{-1} shows the presence of —C—O— groups (which are also contained in carboxylate groups). The peak of delocalized C—C double bonds persists, but its second maximum at 937 cm^{-1} is weak and overlapped with another peak. The new peak at 624 cm^{-1} shows the possibility of the formation of oxidic phase. The position of its maximum is somewhat shifted in comparison with the maximum corresponding to SnO_2, so it may be concluded that suboxidic SnO_x ($x < 2$) phase is formed. For further details, see Figure 4.

Figure 5 is a spectrum of pure tin dioxide with a single strong absorption peak at 657 cm^{-1}.

Figure 6 compares spectra of layers deposited at energy densities ranging from 0.15 to 1.5 J cm^{-2} with pure SnAcAc (upper one). It can be generally concluded that the similarity of the deposited layer spectrum to that of pure SnAcAc decreases with increasing energy density of laser radiation. The strongest absorption maximum at 1536 cm^{-1} and the double peak at 1023 and 937 cm^{-1}, which are typical for acetyl acetonates, are

retained only at 0.15 and 0.3 J cm^{-2}. On the other hand, the peak corresponding to ν(—C—CH$_3$) at 1282 cm^{-1} is present in all cases. At the energy densities higher than 0.3 J cm^{-2}, a detectable quantity of SnO_2 is formed (maxima about 657 cm^{-1}). To characterize these changes more exactly, we decided to evaluate the ratio R = (absorbance at 937 cm^{-1})/(absorbance at 657 cm^{-1}). The higher the value of this ratio, the higher the similarity to acetyl acetonate. Table I summarizes the values of ratio R for the layers deposited at energy densities ranging from 0.15 to 1.5 J cm^{-2}.

The FTIR spectra of the layers deposited at various working atmosphere pressures are depicted in Figure 7. The deposition time was 5 min in all cases. These spectra at 10, 30, and 100 Pa are almost identical with the upper one corresponding to pure SnAcAc. They represent the best results among other experiments from the point of reproducibility of chemical composition. It was suitable to use the same quantity (R) for the characterization of acetyl acetonate similarity as
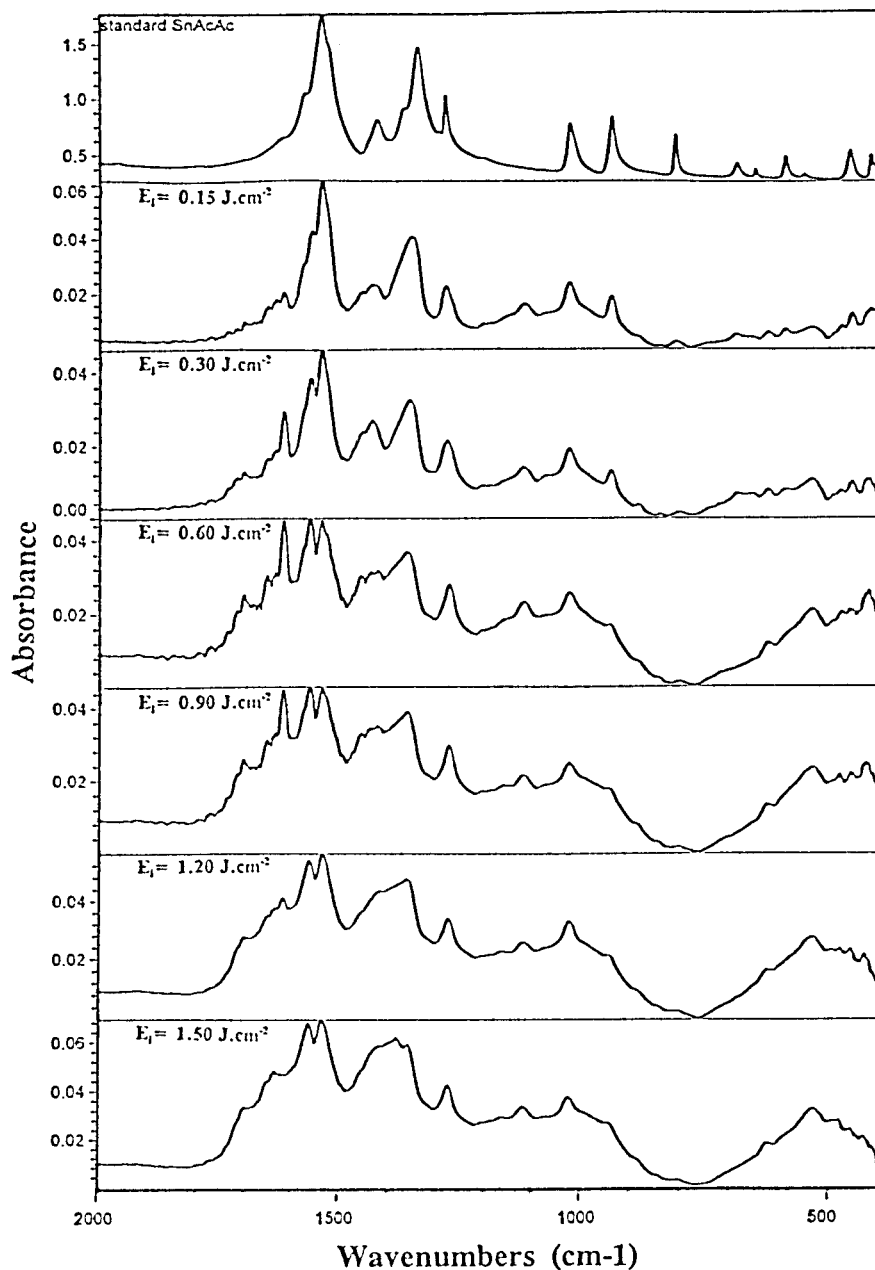
Figure 6   The comparison of the layers deposited at distinct energy densities ranging from 0.15 to 1.5 J cm^{-2} with pure target SnAcAc (upper spectrum).

in the previous case. The corresponding values of R are summarized in Table II.

X-Ray Photoelectron Spectroscopy

Figure 8 presents O_{1s} spectra of distinct materials and layers (starting from the bottom): bulk tin dioxide, bulk tin acetyl acetonate, the as-deposited SnAcAc layer ($E_l = 0.6$ J cm^{-2}), and the same layer after thermal activation. The binding energy of 531.0 eV corresponds to oxygen bonded in SnO$_2$, whereas the binding energy of 532.6 eV

represents oxygen atoms bonded in carbonyl groups of acetyl acetonic ligand cycles. The line corresponding to as-deposited SnAcAc layer is strongly asymmetric, but it is apparent that oxidic oxygen clearly dominates in this case. The asymmetry is caused by the presence of carbonyl oxygen, but its content is estimated to be only about 10%. Finally, after thermal activation, the O_{1s} line is rather weak. In contrast to the previous case, the carbonyl oxygen prevails after the activation process. This is probably due to the

Table I   The Dependence of Values of Parameter *R* Versus Energy Density of Laser Radiation for Distinct Layers

Energy Density of Laser Radiation E_l (J cm^{-2})	Value of R (dimensionless)
pure SnAcAc	15.0
0.15	6.0
0.30	2.4
0.60	2.3
0.90	2.1
1.20	1.8
1.50	1.8

All of these layers were deposited in nitrogen atmosphere (working pressure 10 Pa).

Table II   The Dependence of Values of Parameter *R* Versus Working Atmosphere Pressure for Distinct Layers

Working Atmosphere Pressure (Pa)	Value of R (dimensionless)
pure SnAcAc	15.0
10	2.0
30	3.6
100	2.2

The energy density of laser radiation (E_l) was 0.3 J cm^{-3} in all cases.

presence of hydrogen in the atmosphere during activation. Hydrogen reduces the tin dioxide almost completely, but not the carbonyl groups. So the content of carbonyl groups is practically the same as in the state before activation, whereas the content of tin dioxide decreases significantly. This spectrum also shows the presence of hydroxyl groups as a result of water vapor adsorption, because the porosity (observed by TEM) of the layer after thermal activation is high.

Figure 9 depicts C_{1s} spectra of the samples in the same order as Figure 8. The main maximum of binding energy at 285.0 eV represents carbon
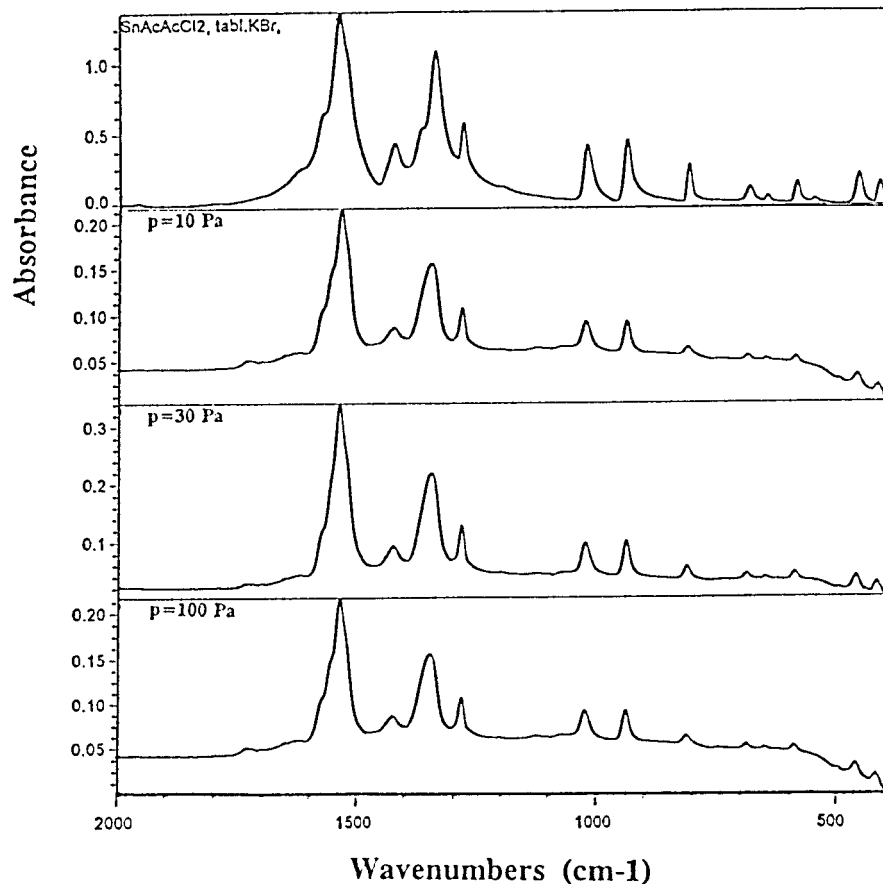
Figure 7   The FTIR spectra of the layers deposited at various working atmosphere pressures (from 10 to 100 Pa) and the spectrum of pure target SnAcAc (upper one).
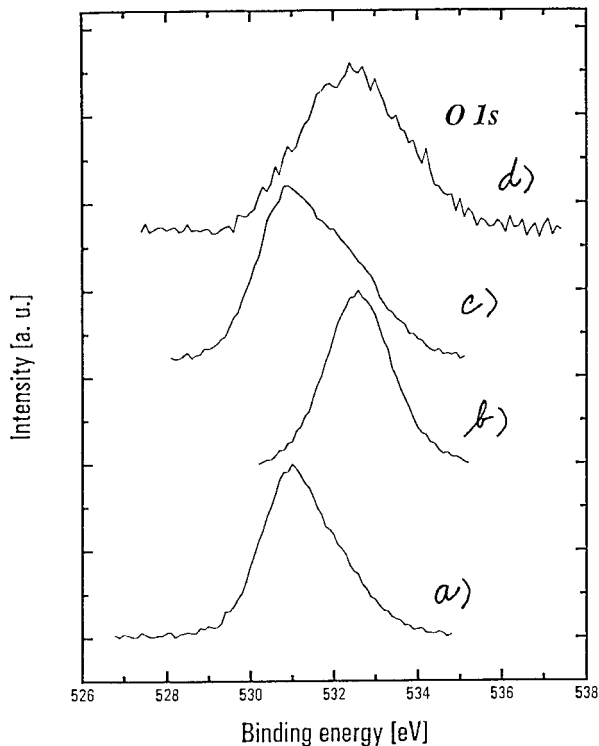
Figure 8   The XPS O_{1s} line of (a) bulk tin dioxide; (b) bulk tin acetyl acetonate; (c) LAD as-deposited layer from SnAcAc target; (d) the previous layer after thermal activation.

atoms bonded with aliphatic single bonds. The adjacent maximum at 287.4 eV in the spectrum of bulk SnAcAc reveals the presence of a carbonyl group in the acetyl acetonate. This maximum persists partially after the deposition, but disappears completely after thermal activation. The thermal activation also leads to a widening of the main maximum, which is connected to graphitization.

The basic conclusions following from Sn_{3d} spectra (Fig. 10) are similar to those from O_{1s} spectra (i.e., there is a significant maximum at 486.5 eV representing tin dioxide). It is dominant in the spectra of both pure tin dioxide and the as-deposited layer. The maximum for tin bonded in acetyl acetonate is shifted to higher energies (about 488.0 eV). The signal is weak after thermal activation at 430°C. Tin dioxide is partially reduced by a hydrogen atmosphere and liquid, metallic tin diffuses to bulk material or evaporates. The rest of the tin atoms remain bonded in the form of complexes with carbonyl groups or carboxylate salts.

CONCLUSIONS

The LAD method with an excimer KrF laser was used for the deposition of thin layers from the

targets of SnAcAc and SnO_2. These layers were analyzed by FTIR and XPS spectroscopies.

The main results follow from FTIR spectra. The content of acetyl acetonic phase was evaluated according to presence of absorption maxima corresponding to delocalized C$\cdots$C and C$\cdots$O bonds, which are typical for coordinative arrangement between metallic ion and acetyl acetonate ligands. The content of oxidic phase was evaluated by comparing with the spectra of pure oxides. In the case of the layers deposited from SnAcAc targets, the content of SnO_2 and suboxides SnO_x ($x < 2$) increased monotonously with increasing energy density of laser radiation. The acetyl acetonic phase predominated at the two lowest energy densities only. In contrast, the deposition at higher working gas pressure (10, 30, and 100 Pa) leads to acetyl acetonate layers with good reproducibility. After thermal activation of the deposited layers, the acetyl acetonic phase was transformed to a system containing cumulative double bonds and carboxylates. Such products have antagonistic effects on the suitability of these layers in chemical sensor technology.
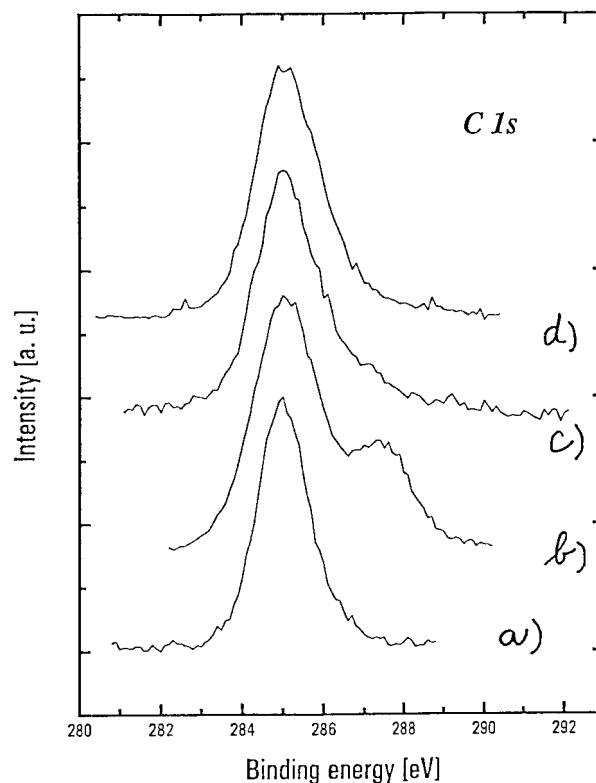
Figure 9   The XPS C_{1s} line of (a) bulk tin dioxide; (b) bulk tin acetyl acetonate; (c) LAD as-deposited layer from SnAcAc target; (d) the previous layer after thermal activation.
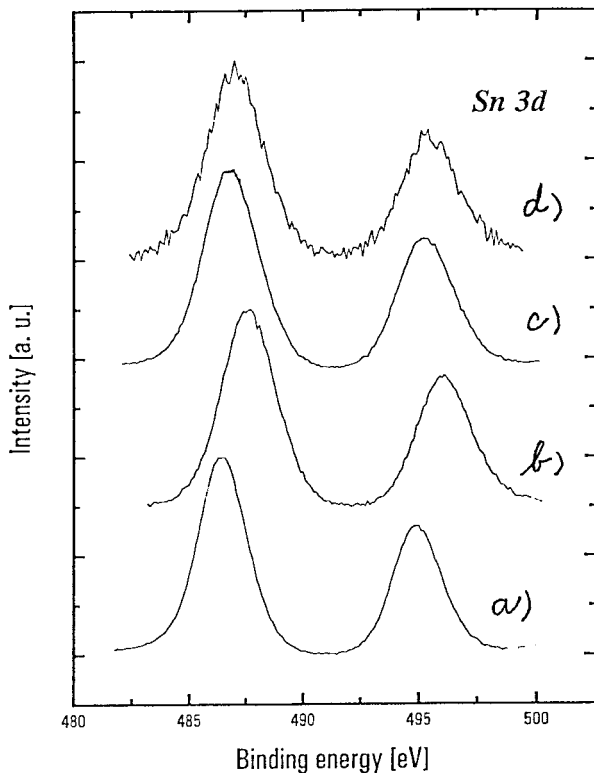
Figure 10 The XPS Sn_{3d} line of (a) bulk tin dioxide; (b) bulk tin acetyl acetonate; (c) LAD as-deposited layer from SnAcAc target; (d) the previous layer after thermal activation.

The main results follow from XPS spectra. It must be taken into account that XPS spectroscopy is a method of surface analysis in contradiction to bulk-analyzing FTIR. It is clear that on the sur-face of as-deposited layers the ratio of amounts of tin acetyl acetonate versus tin oxides SnO_x is approximately 1 : 9. During the thermal activation of deposited layers, the following processes take place. (1) Tin oxides are reduced by hydrogen contained in activation atmosphere; (2) tin acetyl acetonate is predominantly transformed to tin carboxylate; (3) carbon chains with conjugated double bonds tend to graphitization.

It can be concluded that laser technology is suitable for preparation of active layers of chemical sensors. Some results concerned with the sensing properties of SnAcAc active layers were published in ref. 5. The sensitivity of a sensor containing the LAD-deposited thermally activated sensing SnAcAc layer reached 27 by using an atmosphere containing 1000 ppm of hydrogen and was further increased by a Pd catalyst to 70.

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