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Simultaneous Transfer of the Components of Complex Oxide onto the Substrate in the Flow of Organic Ligand

OLEG V. POLYAKOV, ARAM M. BADALYAN and VYACHESLAV I. BELYI

Institute of Inorganic Chemistry of Siberian Branch of the Russian Academy of Sciences,
Pr. Akademika Lavrentyeva 3, Novosibirsk 630090 (Russia)

Abstract

A new technique of the deposition of the films of complex compounds is presented. This technique broadens the MOCVD (Metal Organic Chemical Vapour Deposition) technology to the case of the simultaneous synthesis-transport. A unique possibility is demonstrated to transfer three metals (components of a complex oxide $Y_1Ba_2Cu_3O_{6+\delta}$) at a time onto a solid substrate, in the form of organic complex in the flow of ligand (β-diketone). The transport of metals was carried out in the ratio close to the initial stoichiometry but with minor deficit of barium.

INTRODUCTION

The simultaneous synthesis and transport (SST) techique proposed by us earlier [1, 2] which is a broadened version of the known technique of the chemical deposition of organometallic compounds from the gas phase (Metal Organic Chemical Vapour Deposition – MOCVD) has several advantages in comparison with the generally accepted version. In particular, one of these advantages is the possibility to generate not only thermodynamically stable but also metastable volatile metal-containing compounds (intermediates) that can be hardly obtained in the individual form for CVD purposes.

The essence of SST technique involves the formation of a volatile metal organic compound (MOC) or metal complex (MC) which is provided in the synthesis zone simultaneously with its desorption from the surface of the grains of non-volatile precursor reagent due to a heterogeneous reaction, in the interaction with the flow of volatile precursor reagent (ligand); the substrate at which further transformation takes place is placed in the vicinity of the synthesis zone downstream the precursor flow. So, this technique unites two technological processes within the same volume: the synthesis of the volatile component and its simultaneous transport on the substrate surface where the target MOC is deposited and decomposed.

The deposition of the components of a complex oxide onto a substrate by means of the traditional MOCVD technique involves usually a complicated synchronization of the performance of several sources of individual MOC (MC) vapours or (in the case of a single source) preliminary synthesis of a volatile polynuclear heterometallic chelate which is a very difficult problem of chemical synthesis. The synchronization of several sources of individual MOCs operating in the SST regime is also a difficult task due to a large number of controlling parameters. Therefore of this, the perspective to use the peculiarities of SST regime in order to transfer simultaneously the metals (constituents of complex oxide), bound in a complex, onto the substrate seems very attractive.

Metal chelates with β-diketones are known to be prone to sublimation in the form of polynuclear complexes. This tendency is especially clear in β-diketonates of alkaline earths like barium dipivaloylmethanate $Ba(DPM)_2$ [3]. The initial stage of the SST process is chemical interaction of ligand molecules with the surface atoms and their detachment from the oxide surface, so it may be profitable from the energy viewpoint to detach them from the lattice of complex oxide. In this case, the process will be characterized by the formation and sublimation of the complex incorporating not only a single atom but an entire fragment including several metal atoms of different types bound *via* oxygen bridges. It is reasonable to propose that this intermediate polynuclear heterometallic complex is metastable and after the deposition onto the substrate it can easily be decomposed, either thermally or photochemically.

The goal of the present study was to demonstrate a principal possibility of simultaneous transport of three different metals, constituents of a complex oxide of the type $Y_1Ba_2Cu_3O_{6+\delta}$ onto a solid substrate, in the form of organic complex in the flow of β-diketone, and to estimate the degree to which the stoichiometry of the initial solid precursor is conserved with respect to metal components.

EXPERIMENTAL

Experiments were carried out with a set-up shown schematically in Fig. 1. A quartz SST reactor [1, 2], modified by us for the possibility of sequential addition of carrier gas through the liquid precursor (ligand), was used. Inside the reactor *1*, in the region of maximum heating of the resistive furnace *4*, the powder containing non-volatile precursor (an oxide or a mixture of oxides) was loaded into a sectional ampoule *5* between two porous glass filters. So, the ampoule loaded with the powder was in fact a short chromatographic column. The temperature of the reaction zone (of the chelate synthesis) T_R was measured by a Chromel-Alumel thermocouple *6* introduced into the zone in a thin quartz tube; temperature was maintained by a thermostabilizer *12* at an accuracy of ~ 1 %. The necessary T_R was varied within the range 150–260 °C above the sublimation point T_S but below the decomposition temperature T_D of the assumed metal complex. If a complex oxide or a mixture of oxides were used, T_R was chosen so that it did not exceed the decomposition temperature of the least thermally stable individual metal complex that could be formed in the system but exceeded sublimation temperature of the least volatile complex [4, 5]. Before heating, the reactor was evacuated with a rough pump till the residual pressure of about 10^{-2} Torr, then the heating in the furnaces was switched on, and the evacuation proceeded for 30 min more. Then the vapour of liquid ligand was admitted into the reactor through the valve 7 and passed through the filling of solid precursor. The tube with liquid ligand *8* was placed in a thermostat *9*; its temperature was maintained at an accuracy of about 1 % and varied within the range 20–90 °C. A short tube *10* was placed in the tube with the ligand; the carrier gas (air, nitrogen) mixed with water vapour was passed through this short tube.

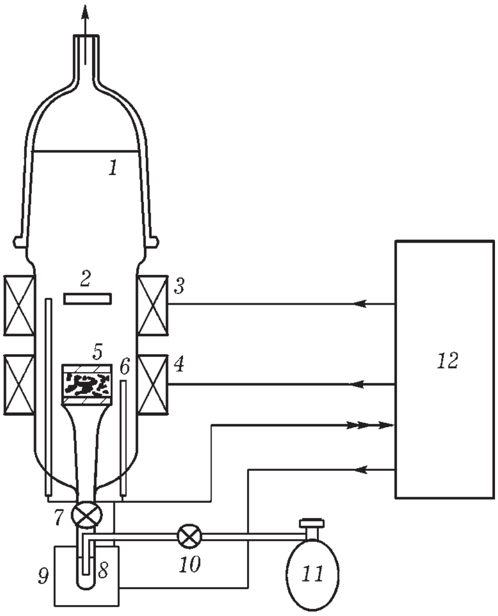

Fig. 1. A scheme of the experimental set-up. For designations, see the text.

A solid substrate *2* was placed along the flow that passed through the ampoule with non-volatile precursor, in the region of maximal heating of another zonal furnace *3* with the temperature stabilized below the sublimation point T_S of the formed chelate but above the evaporation temperature T_E of the volatile precursor (liquid ligand). So, at the substrate, the conditions were created for the evaporation of MC molecular crystals as thin films ~ 100 to 10 000 Å thick.

Ligand carriers were acetylacetone (HAA, pentane-2,4-dione), dipivaloylmethane (HDPM, 2,2,6,6-tetramethylheptane-3,5-dione), and DPM-like methoxylated β-diketones ($HZIS_1$, 2-methoxy-2,6,6-trimethylheptane-3,5-dione and $HZIS_2$, 2,6-dimethyl-2-methoxyheptane-3,5-dione). Barium derivatives of these ligands are highly volatile and thermally stable [5]. Non-volatile precursor reagents were both individual and mixed hydroxides or oxides of yttrium, barium, copper, nickel, cobalt – $Me(OH)_x$, Me_yO_z, and the powder of yttrium-barium cuprate $Y_1Ba_2Cu_3O_{6+\delta}$ Prepared for the agglomeration of voluminous samples of superconducting ceramics.

Before being loaded into the reaction column, non-volatile precursor was mixed with a solid inert loosening substance (activated carbon, sibunite, Polysorb-1, Al_2O_3, SiO_2) in the ratio 1 : 4 (as a rule); in some experiments H_3BO_3 was added as a solid activator. Polished plates of silicon, germanium, sapphire, and quartz were used as substrates.

Express analysis of the synthesized chelate films was carried out using the electron and vibration absorption spectra recorded with optical spectrophotometers operating in the UV or IR regions, as well as using the data of voltammetric analysis of the washing-off solutions obtained by washing the deposited films with aqueous-ammonia solvents. Additional analysis of some selected samples was done by means of X-ray photoelectron spectroscopy, and differential dissolution using emission spectroscopy of the inductively bound plasma [6].

RESULTS AND DISCUSSION

In the case when the powder of an individual solid was used as non-volatile precursor, reproducible transfer of all the mentioned metals as β-diketonate chelates onto a solid substrate was observed. The formation of β-diketonate chelates was unambiguously followed by means of UV and IR spectra of the compounds deposited onto the substrates. In the case when yttrium-barium cuprate was used as non-volatile precursor, simultaneous transfer of all the three metals onto the silicon substrate was achieved.

The quality of the deposited films was substantially dependent on the regimes of ligand admission and on the composition of the gas flow. Smooth glass-like films were obtained when the ligand was transferred in water vapour flow. As it was expected, water molecules play the role of the activator for the cuprate and substrate surfaces, as well as the donor adduct-forming agent. Metal complexes forming the resulting films remained volatile also after the deposition: when kept at room temperature in the air, the films disappeared by sublimation into the atmosphere. It can be assumed that the instability of these films is due to the specific features of their structure and the presence of water in the resulting chelate molecules. We did not carry out direct X–ray analyses of the films but optical absorption spectra suggest indirectly that the structure of molecular crystals is substantially disordered and defect-rich which is likely to be natural for vacuum deposition of the films of polynuclear mixed-metal chelate complexes.

Figure 2 shows UV and IR absorption spectra of these films compared to the corresponding spectra of individual complexes. One can see that a characteristic band at 40 000 cm^{-1} corresponding to the charge-transfer transition of copper chelate complex is absent from the UV absorption spectrum of the resulting film. At

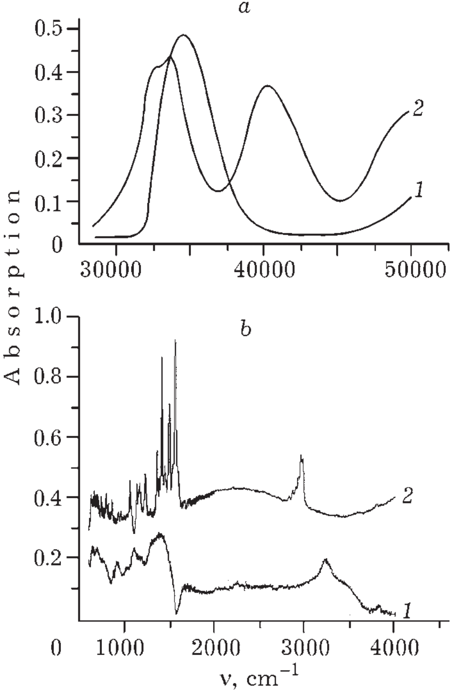

Fig. 2. UV (*a*) and IR (*b*) absorption spectra of the films deposited from yttrium-barium cuprate by the ZIS_2 ligand by means of the combined synthesis and transport (*1*) and from $Cu(ZIS_2)_2$ by means of vacuum thermal deposition (*2*).

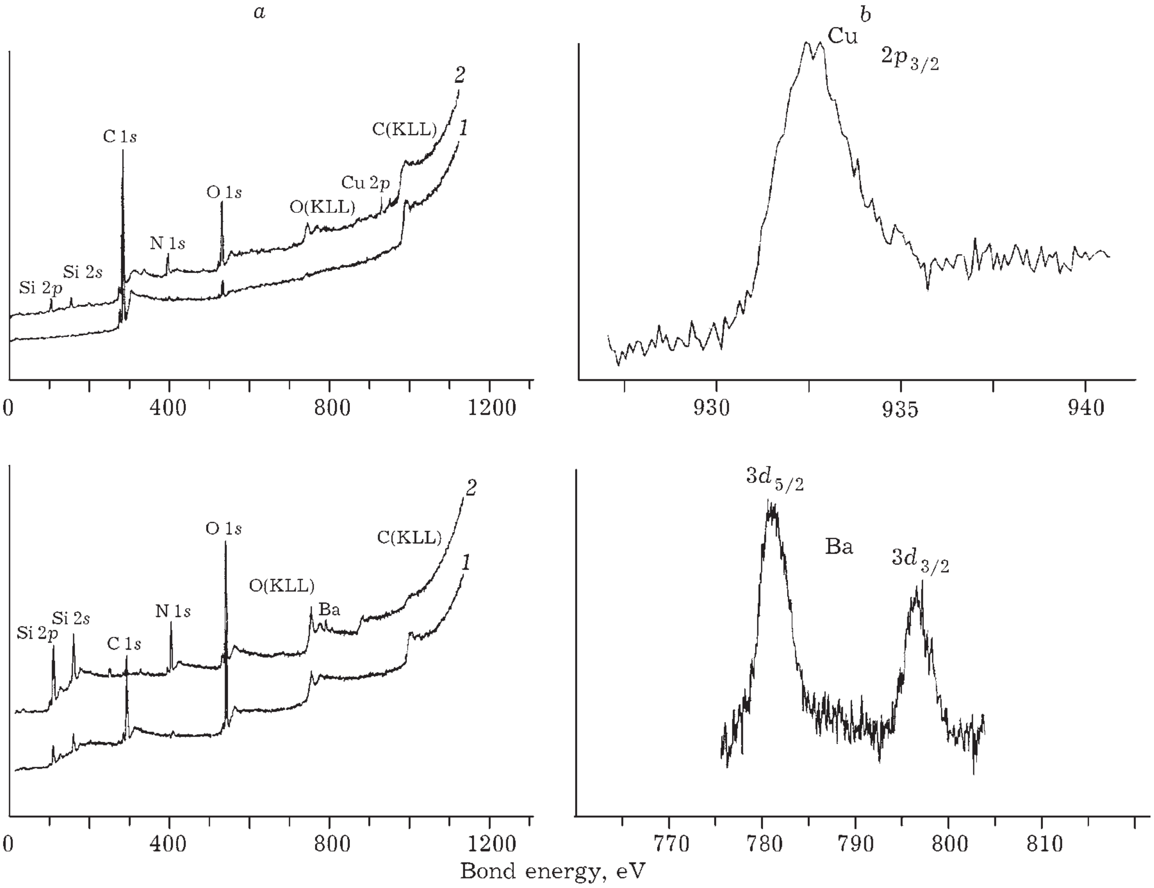

Fig. 3. X-ray photoelectron spectra of the surfaces of two films deposited from yttrium-barium cuprate on silicon substrate by means of the combined synthesis and transport: *a* – overall spectra (*1* – initial film, *2* – the film after the action of Ar ion beam); *b* – the lines of elements.

the same time, the presence of copper in the film is reliably demonstrated by means of the stripping voltammetry. Taking into account the sensitivity of charge-transfer transition to the transformations of the nearest coordination sphere of metal in chelate complex, one can assume that the film incorporates hydrated strained molecular-crystal species composed of polynuclear mixed metal chelates.

The observed features of the IR absorption spectrum of the film, namely, substantially diffuse character of the absorption bands in the regions of stretching vibrations ($C=C$, $C=O$, C—H) and bending ones (C—H) correspond to this assumption. The observed distortion of the IR spectrum could be considered as the evidence of the absence of β-diketonate ligand, either free or bound in metal complex, but the presence of a band characteristic of β-dicarbonyl chromophore points to the presence of two $C=O$ bonds in β-position with respect to each other. In any case, even if a structural transformation of ligand molecules occurs during the surface reaction, independently of the details of ligand structure after the assumed transformation, the transfer of metals as complexes onto the substrate is achieved; the complexes conserve substantial volatility after the deposition.

X-ray photoelectron spectra of the films deposited by means of SST onto silicon substrates using the $HZIS_2$ ligand also exhibit the presence of copper and barium (Fig. 3); however, the situation is in some cases ambiguous. Because of rather complicated structure of the film and its surface, different overlapping structural fragments occur in the zone of X-ray beam. Because of this, XPS spectra of the samples studied by us contain the peaks of either copper or barium, along with the peaks corresponding to organic compound, while the stripping voltammetry of solutions obtained by washing these films points clearly to the presence of copper. The determination of yttrium and barium by means of voltammetry is hindered due to high negative half-wave potential of these elements.

Differential dissolution technique [6] was found to be most informative for the control of elemental composition of the films. This method allows simultaneous analyses, both qualitative and quantitative ones, of several chemical elements including Y, Ba and Cu using the ICP emission spectra of the film dissolved layer by layer. Typical samples of smooth glass-like films obtained by the transfer of the components of the complex oxide $Y_1Ba_2Cu_3O_{6+\delta}$ in the flow of $HZIS_2$ ligand have been analysed by this method. Typical characteristics of the film are: thickness, 1.1 μm (for the deposition time of 60 min); total metal content, 23 μg; Y:Ba:Cu molar ratio in the sub-surface layer, 1 : 1.24 : 3.95; within the film: 1 : 1.22 : 3.08 which is close to the initial stoichiometry with some deviation for barium. Layer-by-layer deposition shows that this ratio is conserved over the whole thickness. This points to the fact that the film is composed of a single phase but not of just a mixture of individual compounds. This fact can be considered as an additional confirmation of the hypothesis concerning the possibility of the transfer of metals from complex oxide in ligand flow as heterometallic polynuclear complexes.

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