New principle of feeding for flash evaporation MOCVD devices

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Abstract - A novel scheme of flash evaporation feeding for MOCVD processes of multi-component oxide films deposition is proposed. The scheme comprises 1) microdosing of organic solution of solid volatile precursors on the glass fiber belt, 2) evaporation of the solvent and 3) flash evaporation of MOC microdoses from the belt. The functioning of the designed feeder is described and the features of proposed scheme in comparison to existing feeding principles are discussed.

1.- Introduction.

In recent years the ability and advantages of CVD technique in obtaining multi-component oxides thin films and coatings was demonstrated not by once. Solid metallurgic compounds (β -diketonates, alcoxides and carboxylates) are normally used as volatile precursors for this purpose. These compounds need heating up to about 100-400°C and low pressure to be sublimed or evaporated, in this connection the technique of CVD with hot vapor sources and hot transport lines is continuously developing. This line of CVD was considerably stimulated by the inquiry of thin films of high-temperature oxide superconductors (HTSC). On the other hand this work revealed some bottlenecks of the technique. Critical currents of HTSC, especially of $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ family being very sensitive to minor presence of impurity phases separating superconducting grains suffer much from deviation of film composition from ideal cation stoichiometry. It is especially so for the films deposited on polycrystalline substrates or single crystals with considerable lattice mismatch (MgO and YSZ are the examples). In case of well-matching perovskite-like substrates (SrTiO_3 , LaAlO_3 , NdGaO_3) this effect is not so drastic due to epitaxy resulting in the displacement of impurity (extra components) on the outer surface of the growing film. Nevertheless surface contamination of impurity phases thus formed is also undesirable because resulting films have rough surface morphology what increases dramatically microwave impedance and excludes the multilayer deposition for SQUID's applications.

2.- Multi- and single source feeding schemes.

The above example demonstrates the importance of precise control of vapor stoichiometry what is difficult to guarantee if the volatile substances are evaporated from three (in case of $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$) or even five (in case of $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{CaCu}_2\text{O}_y$) separate sources. As it follows from the experience it is necessary to mantling the temperature of each source and carrier-gas flow trough it with the very high accuracy (0.1°C and 1% correspondingly) what makes such feeding systems overcomplicated and expensive. Moreover, quite poor reproducibility of volatility of some MOC (especially containing alcaly-earth) and their tendency to decompose or to form oligomeres during evaporation run also make control of vapor stoichiometry unreliable.

The above considerations are the starting point to the development of single source CVD processes. In CVD with aerosol feeding which is the version of such processes one use an organic solution containing volatile compounds of all metal components of the film [1]. The aerosol produced from this solution by pneumatic spraying or ultrasonic nebulizing evaporates in heated transport lines or in the vicinity of the heated substrate. This process being very convenient in respect of component dosage and control of feeding rate is not however universal because of presence of solvent vapor in the deposition zone. Oxidation of the vapor, strongly depending on many process factors such as deposition temperature, total pressure, flow rate, oxidant/organics ratio etc, hampers temperature control of deposition and produce carbon dioxide. The latter dramatically influences on the deposition process if barium or other algal earth are among the components to deposit as it is in case of HTSC materials [2].

Flash evaporation of small particles of a mixture of solid precursors is another approach to single source CVD [3]. Normally one effectuate flash evaporation by dropping small particles onto a heated surface, the temperature being sufficient for evaporation of the less volatile component of the mixture. This feeding principle has an advantage of easy maintaining of vapor stoichiometry and lower requirements to thermal stability of precursors because their reside in the hot zone of evaporator only a few seconds. However microdozage of solids is very sensitive to particles size, humidity and cohesion. As a result simple dropping feeders does not provide both constant and low feeding rates.

3.- Principle and functioning of the feeder.

In this paper we propose a new principle of feeding for CVD devices using solid MOC precursors. The feeder designed being a version of flash evaporator combines its advantages with the possibility of precise microdozage in liquid state. A mixture of volatile precursors taken in needed ratio is dissolving in appropriate solvent. The small drops of the solution obtained are dripped on the glass fiber cartridge belt. After the desired mass of the volatile substances is accumulated by consecutive dripping on a section of the belt, the elimination of the solvent by slight heating of the section is carried out and the solution is dripped on the next sections at regular intervals (1.5 cm). The cartridge belt **1** (Fig.1) with the series of dried specks **2** consisting of MOC being put in the evacuated chamber of the feeder is removed with step-motor unit **3**. The belt is moved beside the open end of the output tube **4** of the feeder. When a speck is in front of the tube, the belt is stopped and pressed

against to the tube end by porous heater 6 through which hot Ar flows. At this moment flash evaporation of MOC's from the speck occurs and the obtained vapor flows trough the output tube to the reactor. After the evaporation period the heater goes back, the belt being liberated continues the movement up to the next stop when the evaporation from the next section occurs. The signal to stop the belt is generated by optical sensor 5 when it meets the marks painted at the same interval as MOC specks along the belt edge. The period of evaporation is regulated by electronic timer.

Fig.1.-Scheme of flash evaporation feeder. 1- glass fiber belt, 2- speck of MOC precursor, 3- step-motor unit, 4- heated output tube, 5- optical sensor, 6- heater.

The proposed scheme possess of all general advantages of flash evaporation feeding such as the possibility to adjust vapor stoichiometry changing the composition of the starting solution, undermining temperature and carrier-gas flow control of evaporator, lower requirements to long period thermal stability of volatile substances. In addition to this a very precise and flexible regulation of feeding rate becomes possible due to variation of the concentration of the solution. As it can be shown by simple calculation the dosage of small quantities needed to form one elementary unit thick film is real. For instance, to deposit one elementary unit thick layer of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ about 10^{-6} grams of mixed $\text{Me}(\text{thd})_n$ complexes are needed (if full deposition occurs). This quantity of precursors contains in one standard droplet ($2.5 \cdot 10^{-2}$ ml) if the solution of the concentration 10^{-3} M

is used. The maintaining of feeding rate constant can be achieved also by dripping equal number of droplets on each section of the belt.

A feature of this feeding scheme is the pulse regime of MOC vapor supply to the reactor while carrier-gas flow is constant. As it was observed in our experiments the surface of the films obtained at pulse regime is usually smoother than that obtained at continuous regime of MOC vapor supply if the feeding rates are comparable. This difference is thought to be due to rather slow diffusion mobility along the surface of the deposit. Evidently the time intervals between following pulses are useful for the substance coming to the surface crystallizes in more ordered way.

In contrast to continuous feeding systems the proposed feeder opens the possibility of obtaining thin film materials of composition varied qualitatively or quantitatively normal to the substrate surface. This can be achieved by dripping corresponding solutions of varied composition on the following section of the belt in consecutive order and can be used for *in situ* preparation of multilayers, buffer or resistant layers.

The functioning of the feeder was tested using triple mixture of complexes $\text{Ba}(\text{thd})_2$, $\text{Y}(\text{thd})_3$ and $\text{Cu}(\text{thd})_2$ taken in stoichiometric ratio to obtain $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ film. Hexane solution was used to put the precursors on the belt. The evaporation process (at 300°C , $V_{\text{Ar}}=6$ lph, total pressure 0.1 torr) was monitored by quartz resonator attached to the heated output tube.

It was found that the change of resonance frequency is very proportional to the number of specks passed through the heated zone of the feeder what confirms the constant feeding rate. Microscopic observation of the belt after the test does not reveal any traces of precursors, e.g. complete evaporation took place. The steady response of quartz was observed practically just at the moment when heater touched the speck. We estimate the time of full evaporation to be well within 1 sec.

The shortest full cycle of the treatment of one speck being composed of reeling time, the time of reciprocal movement of the heater and evaporation time was 4 sec. To re-reel 5 m long cartridge belt with 250 specks what is enough to deposit $\approx 1 \mu\text{m}$ thick film the period of 30 min was needed.

The problem of long period open state storage of cartridges with dripped specks can arise due to hydrolysis or carbonization though it was not yet checked experimentally. In that situation adducts of thd-complexes which are more stable against ambience than pure ones can be used [3].

Finally it is to be noted that the design of flash evaporation feeder with infinite belt (instead of rechargeable cartridge) based on the principle described in this paper is in progress.

4.- References.

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