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## NANOSTRUCTURED FILMS OF REFRACTORY MATERIALS PRODUCED BY ULTRA-SHORT PULSE LASER DEPOSITION

R. Teghil, A. De Bonis, A. Galasso, P. Villani

*Dipartimento di Chimica, Università della Basilicata, Via N. Sauro 85, 85100 Potenza – Italy*

A. Santagata

*IMIP – CNR, Unità di Potenza, Via S. Loja, Zona Ind., 85050 Tito Scalo (PZ) – Italy*

**Abstract :** *Thin film of different refractory materials such as carbides, oxides and borides can be successfully deposited by ultra-short pulse laser deposition technique. These films show a nanostructure formed by nanoparticles or nanowires. The possible ablation-deposition mechanism is related to the direct ejection of nanoparticles from the hot target.*

### 1. Introduction :

Pulsed laser deposition (PLD) is a well known technique largely used to obtain thin films of materials with technological interest [1]. In recent years the increasing availability of ultra-short pulse lasers has opened new possibilities. In fact the results, obtained from PLD performed by lasers operating in the fs regime, have evidenced the possibility to deposit stoichiometric films also in the case of systems difficult to deposit by conventional PLD [2,3]. Another interesting feature of the coatings deposited by ultra-short PLD is the presence of a large number of particles with nanometric size [4,5]. In this paper the mechanisms leading to the film formation, together with the possibility to control the coating nanostructure and composition will be discussed.

### 2. Experimental :

The PLD apparatus consisted of a stainless steel vacuum chamber, evacuated to a pressure of  $1.5 \cdot 10^{-4}$  Pa, equipped with a rotating target and a heatable substrate holder. The laser source was a frequency doubled Nd:glass laser ( $\lambda=527$  nm,  $\tau=250$  fs, 10 Hz repetition rate). To analyze the plasma characteristics Optical Emission Spectroscopy (OES) was used while the deposited films were analyzed by the conventional techniques used for the solid state (SEM, TEM, XPS, XRD).

### 3. Results and discussion :

An important feature of the films deposited by ultra-short PLD is their morphology. In fact, these films seem to be formed by the coalescence of a large number of nanoparticles, independently from the characteristics and composition of the starting material (Fig.1) [3,6-12]. The origin of the particles is still matter of debate but their importance in thin films formation is confirmed by the

study of the first steps of the deposits growth showing a large number of particles with a mean diameter in the range 20-50 nm [6,7,11,13]. About the films composition, in some cases the target

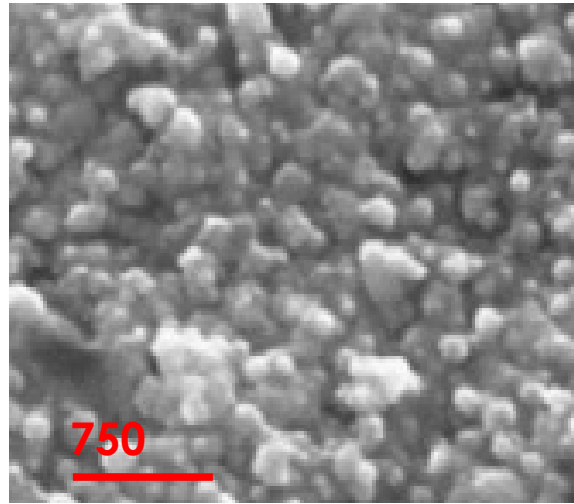


Figure 1. SEM microphotograph of a ZrB<sub>2</sub> film, deposited at 300 °C with a laser fluence of 2.6 Jcm<sup>-2</sup>. From ref. [26].

stoichiometry is correctly transferred to the deposit while in others the film composition is different [6,7,11,14]. These different behaviors could be interpreted considering molten particles, ejected directly from the melted target, as the main constituents of the films. There are several experimental evidences about the presence of molten material on the target surface [8,11] and in the expanding plume [15]. In this hypothesis the melt should have the target composition and also the initial composition of the ejected droplets will be the same. Therefore, every variation of the particles stoichiometry will depend on the composition of the material evaporating from their surface during their flight, lasting several tenth of microseconds, towards the substrate. In metal alloys the melt retains no memory about the structure of the starting solid and under these conditions, the material loss will actually depend only on the vapor partial pressures of the different elements present in the droplets [5,13]. So it is not difficult to predict the composition of the deposited films if the needed thermodynamic data should be available or estimated in the whole range of temperatures. When we consider molecular systems the material loss of the particles, and so the films composition, will depend on the vaporization thermal equilibriums established on the particles at the different temperatures. In this paper we will consider three different types of molecular refractory materials: carbides, oxides and borides. As already seen, the films obtained by ultra-short PLD of the carbides of transition elements do not always show the same stoichiometry of the target. The stoichiometry is preserved in the case of group 4 elements carbides (TiC, ZrC and HfC) [11,16,17] while this is not true for those of the group 5 (TaC and VC). In fact, in these two last cases the films stoichiometry corresponds to the hemicarbides Ta<sub>2</sub>C and V<sub>2</sub>C [7,17,18]. These differences could be explained considering the different thermodynamic behaviors. Group 4 carbides melt without decomposition and their vaporization results to be congruent independently from temperature [19]. On the contrary, for TaC at high temperatures a preferential loss of carbon takes place during vaporization but when the stoichiometry reaches the value corresponding to Ta<sub>2</sub>C the vaporization becomes congruent [22]. Therefore, when the particle composition reaches this value the stoichiometry will not change anymore. The case of VC is not well defined because its thermal vaporization is still matter of debate [19-22]. If we consider the oxides the situation is very similar. To make only one example, the ultra-short PLD of V<sub>2</sub>O<sub>5</sub> can be explained by the same mechanism already proposed. The films deposited by ultra-short PLD of vanadium pentoxide target are formed by a mixture of V<sub>2</sub>O<sub>5</sub> and VO<sub>2</sub>. The thermal equilibriums involving vanadium oxides are quite

complex and strongly temperature dependent, but free energy calculations (Fig.2) show that in the temperature range of our PLD experiments (3200-2800 K) the  $V_2O_5$  and  $VO_2$  liquid phases have comparable stability, indicating in this way the composition of our droplets. In the same way we can explain the ultra-short PLD of several diborides of transition elements. In fact, for this type of materials this technique seems to work very well and several compound, including  $ReB_2$ ,  $RuB_2$  and  $ZrB_2$  have been successfully deposited [3,23,24]. Since there are no thermodynamic data on the first two compounds we will consider only  $ZrB_2$ . At 2500 K  $ZrB_2$  vaporizes congruently and the same behavior is expected for higher temperature [25]. Since the temperature of the particles in our case is 3800 K at the beginning of the flight, the congruent vaporization explain very well the preservation of the target stoichiometry in the deposited films.

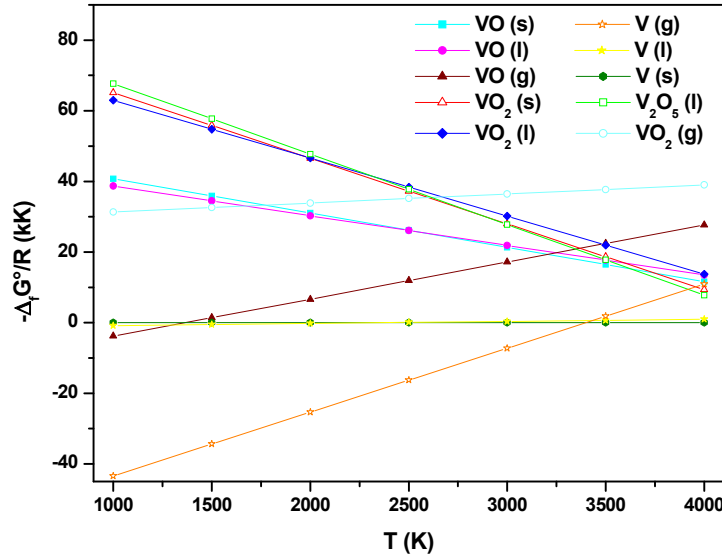


Figure (2) : Negative standard free energy of formation of the vanadium oxides as a function of the temperature.

The choice of these three systems has not been casual. In fact, with the exception of carbides, all these materials are impossible to deposit by conventional PLD, since there is a strong loss of the most light elements, namely oxygen and boron. Another important feature of the films deposited by ultra-short PLD is their nanostructure, formed in general by nanoparticles but in the case of vanadium oxide it is possible to obtain also nanowires. By the interaction of the ablated material with a second laser beam, it is possible to obtain some control about the particles dimensions, even if this procedure could modify the particles stoichiometry. In fact, the effect of the second laser is a re-heating of the particles, with a reduction of the dimension distribution but with also an increase of the temperature that could modify the thermal equilibriums. Anyway, the characteristics of the nanostructured films seem to be very interesting from a technological point of view.

#### 4. Conclusions :

In conclusion ultra-short PLD can be used successfully to obtain nanostructured films of materials with technological interest, such as carbides, borides and oxides. In many cases these films cannot be obtained by conventional PLD and, in any case, the presence of a nanostructure give them peculiar characteristics.

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