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Chemical Vapour Deposition and Atomic Layer Deposition of amorphous and nanocrystalline metallic coatings: towards deposition of multimetallic films

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Abstract

This paper provides a prospective insight on chemical vapour deposition (CVD) and atomic layer deposition (ALD) as dry techniques for the processing of amorphous and nanocrystalline metallic thin films. These techniques are part of major technologies in application fields such as microelectronics, energy, or protective coatings.

From thermodynamic analysis, areas of investigation to generate a set of materials with the strongest propensity for amorphization as well as useful guidelines for the target phase material deposition are provided.

Prospective to develop MOCVD (metalorganic chemical vapour deposition) and ALD of intermetallic films, in view of fabrication of metallic glass thin films is proposed. Examples from selected ALD and MOCVD single element metallic deposition processes will be described to illustrate the effect of deposition parameters on the physico-chemical properties of the films. This processing approach is particularly promising for metallic glass thin films.

1. Introduction

With their excellent mechanical properties [1,2] metallic glasses are expected to offer a broad potential of applications as structural materials. Recently, due to their intrinsic amorphous structure and the consequent linear and planar defect-free character, metallic glasses are investigated to be used as 3D micro/nano structures in micro–and/or nano electrochemical systems (MEMS/NEMS) [3]. The mechanical behavior of sub micronic to micronic pillars made of bulk metallic glasses has been studied [4,5]. Experiments were performed to evaluate size effects in the deformation mechanisms in the amorphous alloys. Work is still in progress to conclude on the existence of a critical size for deformation mechanism and this question is still being debated. Focused Ion Beam (FIB) machining is used with the aim to develop mechanical testing of metallic glass at the micro and nano-scales (below 1 μm) and to fabricate nano-scaled metallic glass samples [4,5]. To avoid any ion damage and ion contamination within a significant nano-scale surface layer originated by this technique which cannot be neglected when the analyzed sample is becoming very small, an alternative route consists in synthesizing metallic glasses in the form of thin films. Till now, among the thin films deposition techniques, physical vapour deposition methods have been exclusively investigated. Different kinds of metallic glass coatings have been deposited, including Zr-Al-Ni-Cu (sputtering) [6], Pd-Si (sputtering) [4], Cu-Zr (coevaporation) [7], Ni-Ti-Zr-Si-Sn (plasma spray) [8].

The aim of this paper is to introduce CVD and ALD as alternative techniques to process metallic amorphous thin films. Compared to physical ones, chemical vapour deposition techniques can be used to provide films with higher purity, better conformality, and more versatility to composition. With CVD techniques, it can be possible to fabricate directly micro-nano pillars by filling up specific matrix trenches. The challenge for this high potential is the necessity to master the complex gas phase and surface chemistries. Moreover, compared to PVD, CVD and ALD tend to produce crystalline phases of metallic materials. Therefore,

CVD of glassy metallic films requires systems with the strongest thermodynamic propensity for amorphization. A thermodynamic analysis will propose more appropriate systems such as Cu-Zr. Examples from selected ALD and MOCVD processes for the deposition of Cu with the effect of deposition parameters on the film physico-chemical properties will be described. Prospectives to develop MOCVD and ALD of intermetallic films, in the view of fabrication of metallic glasses thin films will be given.

2. Thermodynamic requirements to metal amorphization

The thermodynamic prerequisites for amorphous metal stability are continuously being defined from the early developments of metallic glasses and debated [9-12]. The objective of these requirements is to frustrate the formation of crystalline phases. By choosing a phase region with compositions and crystal structures which do not tolerate stoichiometric deviations, the probability that a random adatom on a given crystalline nucleus will be suitable for growth of the crystal decreases. From thermodynamic information, it is possible to predict the propensity of a system to amorphization. For instance, the Cu-Ni phase diagram (figure 1a) indicates continuous solid-solution (and miscibility gap at lower temperatures) that exclude the possibility of amorphous phase formation while the Cu-Zr system (figure 1b) with line compounds [13] meets all the requirements.
Starting with these examples, we will describe the results obtained on selected processes of copper films and the challenges to be met in order to achieve deposition of zirconium films and finally Cu-Zr films.

3. MOCVD and ALD deposition of Cu films

Several metals have been deposited by CVD and ALD processes. We present in this paper some interesting results concerning the deposition of pure copper metallic films.
Due to the predominant position of Cu films in the microelectronics industry, numerous works have been devoted to the MOCVD of Cu. Several families of CVD and ALD precursors have been introduced. Recent work for the MOCVD of Cu from the copper (I) aminidate precursor ($[Cu(i\text{-}Pr\text{-}MeAMD)]_2$ shows the positive effect of the temperature on the film crystallization (**Error! Reference source not found.**) [14]. Particularly, for lower deposition temperatures at 200°C, the size of the crystallites is smaller than 20 nm. Low deposition temperatures promote amorphisation of the fabricated material.

Several studies of copper deposition were carried out by ALD. In the case of using CuCl as precursor [15], zinc was used as reducing agent causing contamination of the thin layer. Moreover, the volatility of CuCl is relatively low, which involves the use of temperatures above 400 ° C to evaporate the precursor and achieve good deposition. The fluorinated copper precursors are attractive because the presence of $-CF_3$ group in the molecule increases the volatility of this family of precursors [16]. However, the presence of fluoride bonds in the precursor may cause fluorine contamination of the layer and deterioration of adhesion due to the diffusion of the fluorine element at the interfaces. The appropriate response to this problem is the use of non-fluorinated precursors. Among those already tested in ALD, the β-cetoniminate and β-diiminate lead to films of relatively pure copper through a reduction with silane or diethylsilane at 50°C [17-18]. Moreover, the family of $[Cu(Amidinate)]_2$ can also be considered to be promising because these precursors are stable and volatile and they lead to deposition of films of pure copper [19-20].

4. *CVD or ALD films of metal with high oxophilicity such as Zr*

Except aluminium (whose deposition has been extensively developed in the seminal book by Kodas and Hampden-Smith [21]) there are but very few reports on the CVD of pure elements presenting a strong affinity to oxygen such as titanium, zirconium. It is due to the difficulty to satisfy the key aspects of the CVD technique in view of the strong reactivity of these elements. Such key aspects include technical limitations of MOCVD reactors and of precursor's delivery systems, but mainly concern availability of appropriate precursors.
Zr organometallic precursors such as TEMAZ (tetrakis(ethylmethylamino)zirconium) or ZyALD (cyclopentadienyltris(dimethylamino)zirconium) or Zr halides such as $ZrCl_4$ have been exclusively dedicated to the deposition of Zr oxide [22] or carbide [23].

However, the chemical vapour deposition of films based on the Cu-Zr systems can be investigated starting from the above-mentioned precursors. Addition of a strong reducer might be a solution.

5. *Concluding remarks*

The scientific and technological field of MOCVD and ALD of metals is actually only partially covered; strong know-how exists on a limited number of metals, among which are found different transition metals (copper, nickel, cobalt). Contrastingly, deposition of titanium, zirconium at zero valence state has only sporadically been reported. Appropriate responses to numerous points have to be provided for MOCVD or ALD process to be tuned with regard to metallic glass deposition: precursor selection, reactors configurations, gas phase and surface chemistry. MOCVD or ALD of multimetallic films are actually in its infancy. This open field is particularly promising and consequently of potential applications with the employment of cutting-edge technology.

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Figure(s)

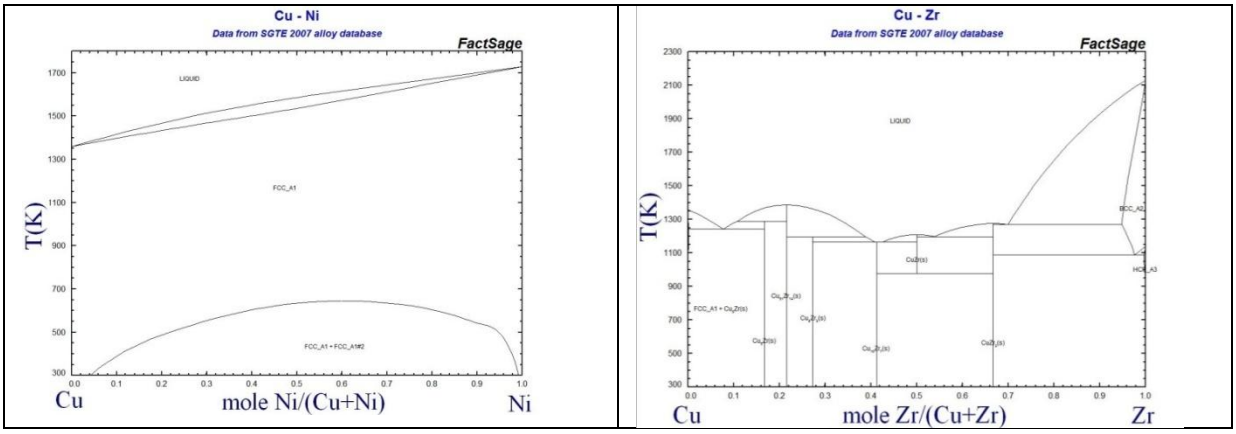

Figure 1 : Binary phase diagrams, Cu-Ni (a), Cu-Zr (b) from [13]

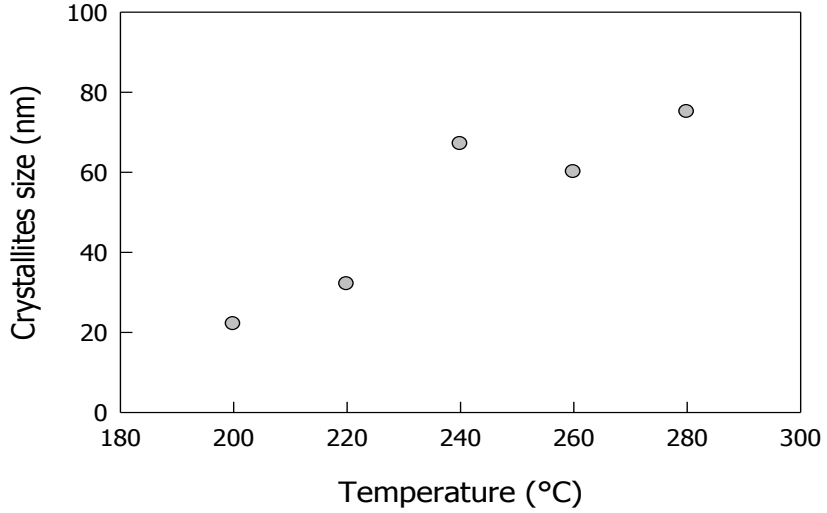

Figure 2. MOCVD of Cu from $[Cu(i\text{-}Pr\text{-}MeAMD)]_2$ on low carbon steel substrates. Estimation of particle size by X-ray diffraction line-broadening as a function of deposition temperature [14].