

Structure and Properties of Sequentially Sputtered Molybdenum-Tin Films

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Sputter deposition has been used for many years to prepare novel multi-component structures. As an example, artificial metallic superlattices containing many layers of two metals deposited sequentially have been extensively studied. The diffusion rates of the freshly deposited species perpendicular to the layers governs the interface sharpness, while rapid diffusion of one or both species along the surface can create mixtures of nanometer or micrometer-sized grains of different phases and completely disturb the superlattice structure. By careful selection of the pair of elements, the layer thickness deposited during each pass under the sputter targets, substrate temperature, etc., it is possible to prepare a wide variety of film structures ranging from amorphous mixtures to well ordered superlattices. For this reason, we selected sequential sputter deposition in our attempts to prepare nanocomposites for lithium-ion battery electrode applications.

Metals that alloy with lithium have been studied as anodes for Li batteries for many years. However, although elements like tin have large capacity for lithium, particles of the alloys crack and fragment during the repeated alloying and de-alloying which occurs as cells are charged and discharged (1). The research groups of Huggins (2) and Besenhard (3) have proposed that alloy fragmentation can be reduced if grain of the active alloying species are embedded in a "matrix" which holds them together. We recently improved on their ideas by preparing nanocomposites of particles consisting of nanoscopic grains of active Sn_2Fe (alloys with lithium) and inactive SnFe_3C (does not alloy with lithium) phases (4). Mechanical alloying was used to prepare the $\text{Sn}_2\text{Fe}/\text{SnFe}_3\text{C}$ active/inactive nanocomposites. Provided that the size of the active grains is only a few nm, the discreet Li-Sn phases in the bulk Li-Sn phase diagram apparently do not form and homogeneous expansion of the active grains occurs as Li alloys with the material. Cracking and fragmentation is prevented and good performance is observed.

It was our opinion that sequential sputter deposition of tin and a second element would give better control over the types of nanostructures that could be prepared. As a first trial, we picked molybdenum as the second element. Tin has a low melting point (232 °C) and Mo has a very high one (2617 °C). Hence, one expects the diffusion rate of the tin atoms immediately after deposition on a room temperature substrate to be much larger than that of the Mo atoms. The fact that Mo-Sn intermetallic compounds exist, suggests that in equilibrium Sn should diffuse into the Mo layers to make homogeneous phases. However, if the diffusion rate of tin parallel to the substrate is larger than the diffusion rate perpendicular (into the Mo) to the substrate, and if relatively thick layers of Sn and Mo are deposited, nanoscopic clusters of tin could form as the tin diffuses parallel to the substrate after each rotation under the tin

target. The tin clusters would be "buried" under subsequent Mo layers. We felt that this could create a very desirable nanostructure for Li battery applications.

Here, we describe the preparation and characterization of sequentially sputtered Mo-Sn films. The major goal of this work is to understand how the nanostructure of the films depends on the deposition conditions. Figure 1 shows a schematic diagram of the nanostructure of such a film.

Another talk presented at this conference will describe the electrochemical properties of the films described here. A further talk will describe the safety and performance of 18650 size Li-ion cells using Mo-Sn negatives.

References

1. Some of the pioneering scientific work in this area has been carried out by the research groups of R.A. Huggins and J.O. Besenhard. See for example, B.A. Boukamp, G.C. Lesh and R. A. Huggins, *J. Electrochem. Soc.*, **128**, 725 (1981); J. Wang, I.D. Raistrick and R.A. Huggins, *J. Electrochem. Soc.*, **133**, 457 (1986) or J.O. Besenhard, J. Yang and M. Winter, Paper Presented at the 8th International Meeting on Lithium Batteries, Nagoya, Japan, June 1996, extended abstracts page 69.
2. R.A. Huggins and B.A. Boukamp, US Patent #4,436,796 (1984).
3. J. Yang, M. Winter and J.O. Besenhard, *Solid State Ionics* **90**, 281 (1996).
4. Ou Mao, R.L. Turner, I.A. Courtney, B.D. Fredericksen, M.I. Buckett, L.J. Krause and J.R. Dahn, *Electrochemical and Solid State Letters* **2**, 3 (1999).

Figure 1. Schematic structure of a Mo-Sn co-sputtered film. The composition is about 50% atomic tin. Layers of 15 Å Sn and 9 Å Mo were deposited sequentially.

