

COPPER DOTS DEPOSITION USING NEW PRECURSORS

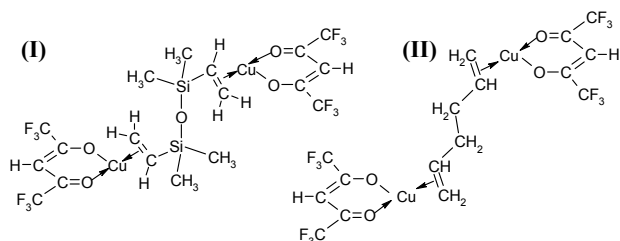
$[\text{Cu}^{\text{I}}(\text{hfac})]_2(\text{DVTMSO})$ and $[\text{Cu}^{\text{I}}(\text{hfac})]_2(\text{HD})$

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Copper dots with various size and shape were obtained under the typical MOCVD operating conditions using new stable compounds of formula $[\text{Cu}^{\text{I}}(\text{hfac})]_2\text{L}$, where L=1,2-divinyltetramethyldisiloxane, DVTMSO (**I**) and L=1,5-hexadiene (**II**). In general, chemical vapor deposition process cannot be used for the formation of Cu nanocrystals because of its high growth rate, which is over the Cu size and shape control range. In this work, we present the new approach for fabricating the Cu nanocrystals by metal-organic chemical vapor deposition through the manipulation of precursor molecular structure.



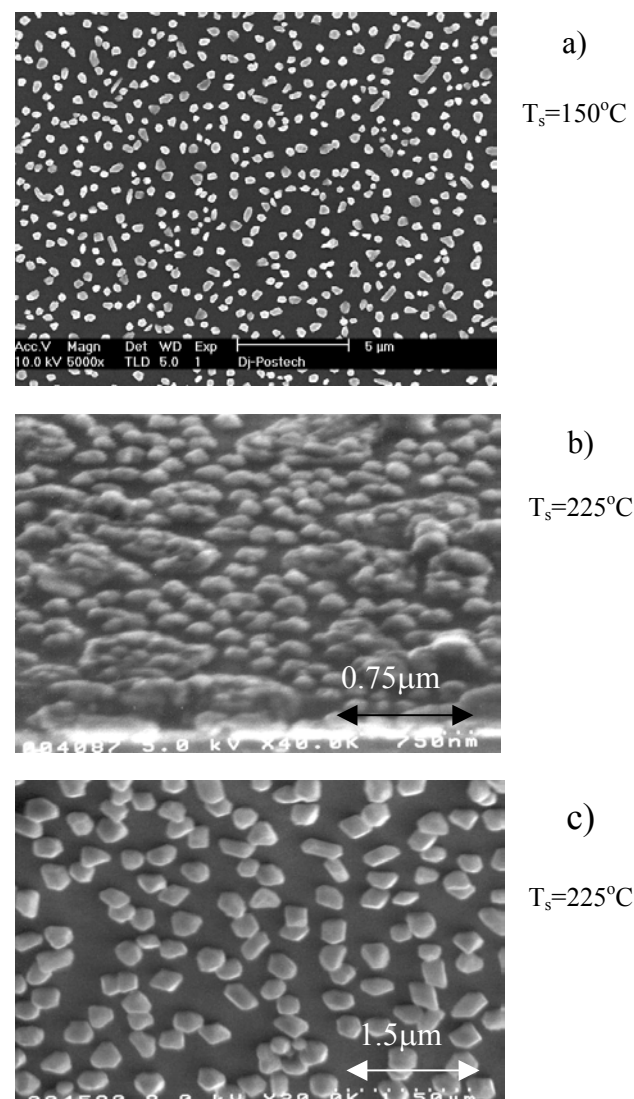
Characterization of New Precursors. Compound (**I**) is yellow crystalline air stable at room temperature, m.p.71°C; compound (**II**) is stable under inert atmosphere compound, m.p.101°C. Both of them can be sublimated at 50–70°C in vacuum. As it follows from TGA and DSC, compound (**I**) is much more stable than (**II**). The new precursors have relatively high vapor pressure when compared to other solid precursor, e.g., (hfac)Cu(COD).

New precursor (**I**) consists of two $[\text{Cu}(\text{hfac})]$ fragments bonded by one bidentate DVTMSO ligand. From the chemical point of view, possible coordination of oxygen atom stabilizes such a structure and results in specific physical-chemical properties of this compound. Compound (**II**) seems to have the same structure but without additional heteroatom and then has different properties.

Copper MOCVD. The continuous copper layer was not formed but only the islands of copper were observed, although the deposition time (20min) is long enough, from the copper MOCVD using (**I**) and (**II**) as precursors. It seems that there is the “prohibitor” to block the formation of continuous copper layer. For example, the ligand such as DVTMSO or 1,5-hexadiene may prohibit the adsorption of copper precursor on the surface or inhibit initial redox process in the molecule. Also long lifetime of the ligand on the surface can prevent further nucleation and accretion of copper islands. As to films morphology, fractal islands with seed at the center point and the branches of copper are observed at substrate temperature of 100°C for both two precursors. However,

at substrate temperature of 150°C, the round-shaped islands of Cu with diameter of 400-700 nm were observed for both two precursors (Fig.1a). And at the substrate temperature of 225°C, the mixed island shape with fractal and round is shown for (**I**) (Fig.1b), but the regular islands are obtained for (**II**) (Fig.1c). It seems that the supply of Cu adatoms on the surface is extremely limited for the two precursors which have two Cu(hfac) fragments and one neutral ligand. It is believed that the reaction mechanism may be changed as a function of substrate temperature resulting in the change of morphology of Cu.

Fig.1. SEM images of copper grown on the TiN substrates.



Conclusions. New method was investigated for the fabrication of copper nanocrystals through the manipulation of precursor molecular structures. From MOCVD process with new copper(I) hexafluoroacetylacetonate complexes with olefin ligands bearing by two vinyl groups, copper islands with various shape and size distribution were obtained and these can be used for the fabrication of copper nanocrystals.