CONTINUOUS AND GRANULAR METAL FILMS PRODUCED BY CHEMICAL VAPOR DEPOSITION WITH CHELATE COMPOUND PRECURSORS

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Thin metal films occupy the important place in microelectronics, magnetic storage and allied domains. The continuous films of Ni, Co, Cu, Mo, W and others are used in microelectronics for ohmic contacts, interconnections and so on. The metal granular films are used for magnetic storage. The granular films with magnetic metallic clusters embedded in insulating matrices attract attention because of it unusual magnetic property.

Widely known the metal organic chemical vapor deposition (MO CVD) process is applied for thin continuous metal film formation. However, for granular metal film formation the polyol process, involving the reduction of metal salt with ethylene glycol or diethylene glycol, and the process of metal and inert gas condensation are used. The aim of this paper is to discuss some points of using the MO CVD process for the continuous or granular metal film formation.

The chelate compounds *bis*-(2-Imino-Pen-En 4-Trifluoro-Acetylacetonato) Ni(II) – Ni(ktfaa)$_2$ and *bis*-(2,2,6,6-Tetramethyl-2,5-Heptandionato) Cu(II) – Cu(dpm)$_2$ were used as precursors for Ni and Cu film deposition, respectively. The films were deposited at 250-350^{0}C using a vertical flow warm-wall reactor equipped with an inner precursor sublimator. The nickel films were deposited onto $5 \times 10 \times 0.4$ mm (100) *p*-Si and $5 \times 10 \times 1$ mm Cu polycrystalline plates (the substrates). The pure Cu substrates were polished up to surface roughness of 0.08 μm. Then the substrates were washed with high-purity acetone, boiling high-purity trichloroethylene, deionized water and dried in air. The copper films were deposited onto $20 \times 20 \times 0.4$ mm sitall (SiO$_2$) plates polished and washed like describe above for Si substrates.

On copper substrates the films are the replicas of the substrate surface at temperatures of 250 – 300^{0}C. The roughness appears only when the film thickness exceeds 120 nm. Hence, the metal films on the metal substrates, at least for transition metals, are continuous. On silicon substrates the granular metal films are deposited. This known phenomenon is associated with the selective metal deposition. The separated metal particles coalesce when the film thickness increases. We can see also that the deposition rate is much more on the copper substrates against the silicon substrates at the same procedure conditions. The films have *fcc* Ni structure according to the XRD data but the only diffraction peak corresponding to d$_{III}$ = 2.03 Å was reliably recorded because of small film thickness. It is clear that the XRD data are associated with the film volume structure. In regard to the structure of a film upper layer the electron diffraction showed the presence of the reflections of the *fcc* Ni structure and a number of additional unknown reflections.

We compared the spectra of the CVD Ni film with the Ni films obtained by the unoil vacuum and oil vacuum sputtering methods. In the latter polyether oil was used. The peak with the chemical shift of +3 eV relative to the Ni^0 peak corresponds to nickel oxide. The wide minor peak at 855.5 eV binding energy is associated with Ni effective charge of +1 which probably corresponds to the Ni – O bond in the Ni(ktfaa)$_2$ chelate. The resistivity of the Ni films on the Cu substrate was less than 5×10^{-6} Ω cm but it may be the result of the bulk copper influence. The resistivity of the Ni film on the silicon substrate was found to be 2×10^{-4} Ω cm that is higher than that of bulk Ni. This can be mainly attributed to the small contact area between the Ni clusters for thin films (50 - 100 nm). What is quite surprisingly that the thin insulator layer exists on the film top independently on the procedure interrupting time, experiment conditions and substrate materials. The insulator property of the film top becomes apparent under electron beam in SEM because of electrostatic charge accumulation on the film surface. The insulator layer was not removed by annealing in H$_2$, dissolving with ether, chloroform and others metal chelate solvents. Only after the delicate mechanical treatment of the film surface the metallic contacts for resistivity measuring may be produced.

The Cu films were deposited on the sitall (SiO$_2$) substrates with Cu(dpm)$_2$ percursors. The granular Cu films are deposited in reduction (hydrogen) and inert (argon) atmospheres at the same others procedure conditions: substrate temperature of 310^{0}C, partial pressure of the Cu chelate of 0.09 Torr. The thickness of the films produced in H$_2$ and Ar equal to 750 and 75 nm, respectively, for the procedure time of 15 min. Hence, the copper deposition rate is ten times greater in the reduction atmosphere. The resistivity of the films 750 nm thick produced in H$_2$ is $(3-5) \times 10^{-6}$ Ω cm and $(7-10) \times 10^{-6}$ Ω cm for 80 nm thick but the film 75 nm thick deposited in Ar showed an insulator property. However, all films had *fcc* Cu structure, according to XRD study. Hence, in the case of the copper deposition in Ar the copper particles had no metallic contacts because of protecting by the insulator layer. The insulator is, probably, an organic by-product of the chelate thermolysis. All Cu films produced at different procedure conditions in H$_2$ were covered by thin insulator layer as in the Ni case discussed above. It seems that for Ni and Cu films we obtained the polychelate formation on the metal surface. The polychelate moves together with film surface during metal granule growth.

According to the experimental data the effective activation energy of the chelate reduction in H$_2$ is 27 ± 7 kJ/mol. The deposition rate is larger at the same temperatures for H(dpm) addition but the effective activation energy is smaller and equals 10 ± 5 kJ/mol. The reaction order with respect to H(dpm) equals zero.

The treatment of experimental kinetic data have allowed to present the multistage reaction scheme of the Cu chelate reduction. One of the stages is a formation of the polychelate, which moves with the metal surface during all process.

The granular film formation is preferred on nonmetal substrates, for example, silicon and silicon oxide plates. In reduction atmosphere the deposited granules increase in size and coalesce during the process, resulting in metal conductivity over the film. In Ar the fine metal granules do not increase in size, their coalesce is excluded and metal conductivity over the film are not realized.