Polycrystalline Copper Whiskers and Networks Observed in MOCVD

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Due to optoelectronic applications and regional economic needs, CVD of copper and related oxide compounds with nano structures have been a long-term research project in our group since 1990s. In a study to explore the CVD of copper chromite ($CuCr_2O_4$) using copper acetylacetonate, $Cu(C_5H_7O_2)_2$ and chromium acetylacetonate, $Cr(C_5H_7O_2)_3$ as precurser. When water vapor, rather than oxygen, was used as co-reactant, we discovered that deposits were fibrous like polycrystalline copper deposits primarily, but not copper chromite. XRD and SEM results show that such fibrous deposits are polycrystalline copper "whisker".

A continued and systematic study show that nano structured copper whiskers can be grow in an atmospheric pressure chemical vapor deposition (CVD) system, which used copper acetylacetonate vapor and 10-15 torr of water vapor as reactants, with 0.04-0.10 torr of chromium acetylacetonate vapor added as growth promoting catalyst. There are some differences between classical vapor grown whiskers and the materials found in the metal acetylacetonate/water vapor CVD system. Classical whiskers are usually single crystal, straight with sharp tips, while fibrous copper deposits were polycrystalline of Cu(111) and (200) orientations. The shape are spiral or helical with round tips. Comparison tests indicated that water vapor initiated nucleation of these whiskers. While chromium acetylacetonate accelerated the growth rate. Narrow scan XPS and Depth profile Auger show that very few Cr were found in films, and most Cr were assumed being distributed between Cu lattices.

SEM showed these copper whiskers had radii from 0.1 to 0.24 μm, lengths from 1 to 10 μm, and distribution density of 0.20-3.6 whiskers/μm^2. Dependence of such growth characteristics on temperature, partial pressures of H_2O and chromium acetylacetonate was used to construct a kinetic model. From the Arrhenius equation, data analysis showed that the activation energy for whisker growth along radial direction is 12.4 kcal/mol, and 19.6 kcal/mol for growth along axial direction. Based on such data and SEM observations, a base vapor-liquid-solid (VLS) model involving BCF theory was proposed to describe the governing mechanism for the axial growth. This model interpreted the competitive growth phenomena in both radial and axial directions, and controlling steps for radial and axial growth being assigned to mass transfer and surface reaction, respectively.

A further study done recently we showed that, by modifying the surface property of substrate, another new nanostructure can be created. As we used pre-sputtered Cu or copper oxide coated Si(100) as substrates, the Cu deposits form three dimensional network structure, rather than one dimensional wires, at the same process condition. We assumed this phenomenon comes from variation in surface composition, which changed nucleation and growth behavior of Cu deposits.

Key words: Cu whisker, copper, acetylacetonates

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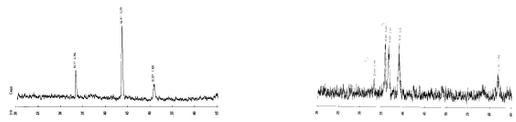
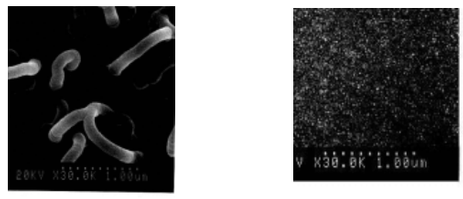
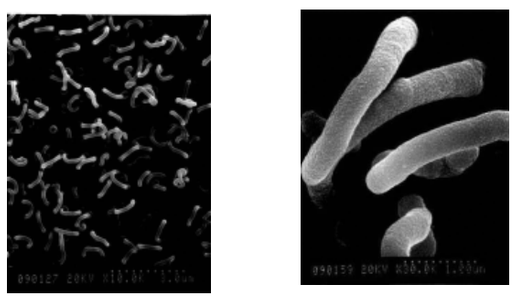


copper whisker **(A)** poly $CuCr_2O_4$ spinel (311) **(B)**



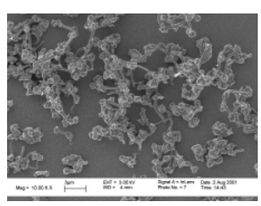
copper whisker **(A)** poly $CuCr_2O_4$ spinel (311) **(B)**

Fig. 1 XRD/SEM of CVD copper whiskers (A) and poly $CuCr_2O_4$ spinel (311) phase (B) both with sublimation temperature: $Cr(acac)_3$: 150°C, $Cu(acac)_2$: 180°C , deposition temperature: 420°C, time 10 min, **with 15 torr H2O vapor (A), or 290 torr O2 (B) as co-reactant**

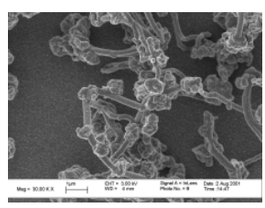


(A) **(B)**

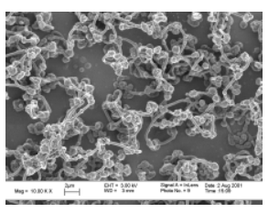
Fig. 2 SEM of CVD copper nano whiskers
Sublimation temperature: $Cr(acac)_3$: 150°C, $Cu(acac)_2$: 180°C , Deposition temperature: **340 °C (A) 420°C(B)**, time 10 min, substrate: blank Si(100) wafer



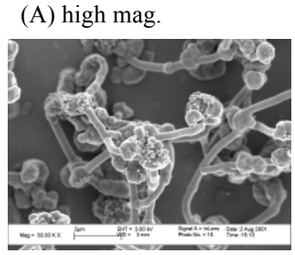
(A) low mag.



(A) high mag.



(B) low mag.



(B) high mag.

Fig. 3 SEM of CVD copper nano networks
CVD precursor sublimation temperature: $Cr(acac)_3$: 150°C, $Cu(acac)_2$: 180°C , deposition temperature: **380 °C (A) 420°C(B)**, time 10 min, substrate: DC sputtered Cu coated Si (100) wafer