MOCVD of Copper/Copper Oxide Nanowires by High Supersaturation Ratio and Seed Layer

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In an MOCVD system, we have discovered a unique nanostructure, wire growth of copper oxide phases causing from high sublimation temperature(> 190°C), that results in high supersaturation of precursor in gas phase, together with pre-sputtered CuO buffer layer. Copper oxides are the precursor materials for superconductor, with applications in optoelectronics, energy industry, and catalysis. Cu_2O has a band gap of 2.1 eV, which falls in the visible wavelength range, and makes Cu_2O as a candidate for solar energy cell. CuO can convert solar energy into thermal energy. Cu_2O is a p type semiconductor ($Cu_{2-\delta}O_{1+\delta}$) with excess oxygen present between lattice atoms. The dissociation of O atoms produces oxygen ions and mobile electron holes. Ambient oxygen concentration can affect hole concentration and conductivity of Cu_2O, such that Cu_2O can be used as gas sensor. Cu_2O is also used for rectifying diodes. The MOCVD experiments were performed in a horizontal tubular reactor under atmospheric pressure. We used oxygen/He mixed carrier gas, with oxygen concentration from 0 to 50%. The sublimation of $Cu(acac)_2$ precursor was 160-190°C. We found that the deposits display unusual nano morphology when sublimation temperature is as high as 190°C. Deposition results show that $Cu(acac)_2$ precursor can be easily deposited onto any kinds of substrate as blank silicon wafer, PVD sputtered Zn wafer, or PVD sputtered CuxO wafer, without any obvious selectivity. Compared with other metal acetylacetonates, $Cu(acac)_2$ show strong adhesion to surface. Cu2p X-ray photoelectron spectra were collected from CVD films to analyze valence of copper ions. As the line position for Cu2p3/2 was at 932eV(Fig.1)； the line width (FWHM) is narrow, without shake up lines, a characteristic of Cu^{2+} ion XPS, which suggest that surface layer of CVD film contains Cu^0 or Cu^{1+} mainly. The Kinetic energy for Cu Auger electrons (Fig.2) from CVD film was 917.6 eV. While the binding energy of Cu2p was 932.2 eV, that yielded an α Auger parameter of 1849.8 eV. As compared with standards, it indicated that Cu^{1+} was the major ion in film surface layer. XRD show that $Cu/Cu_2O/CuO$ mixed films were deposited at a total carrier gas flow rate of 40 sccm, oxygen concentration of 10-50%, and deposition temperature from 360 to 400 °C. The primary grain orientations were Cu_2O (111), and Cu_2O (200)(Fig.3). For films deposited at [O_2] from to 20 to 40%, sublime temperature 190°C, and deposition temperature 400 - 440 °C, SEM (Fig. 4,5) and XRD results indicated that films were composed by one dimensional Cu(111) phase nano wire with average diameter 0.3-0.5 μm, length 3-5 μm, and density 1.4 /μm^2. These nano wires have a round rod shape. But few other SEM (Fig 6,7) show films deposited at similar process range were composed by one dimensional Cu_2O (111) phase nano wire with average diameter 0.5-0.55 μm, length 2-3 μm, and density 3/μm^2. It seems that the growth competition is vigorous. We proposed one preliminary model suggesting that excessive precursor vapor cause high concentration of acetylacetone, released from $Cu(acac)_2$, stay on the surface, causing self redox reaction of Cu_2O and formation of new Cu(111) phase. The Cu(111) phase then acts as nucleation and growth site for subsequent nanowire.

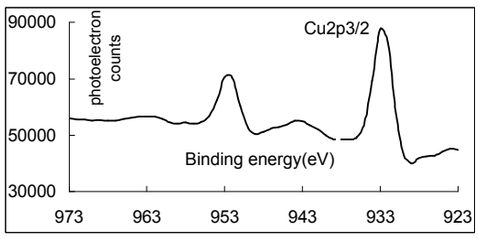

Fig.1 XPS of Cu2p in CVD film [O2] = 25%, 400°C

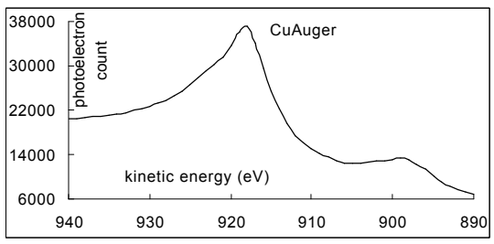

Fig.2 XPS of CuAuger in CVD film [O2] = 25%, 400°C

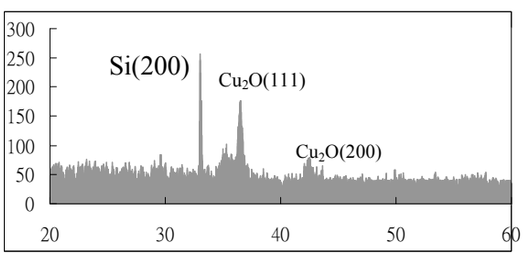

Fig.3 XRD of CVD film [O2] = 25%, 400°C

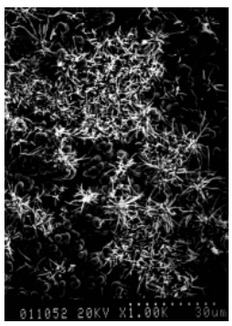

Fig.4 SEM of CVD film [O2] = 25%, 440°C low magnification

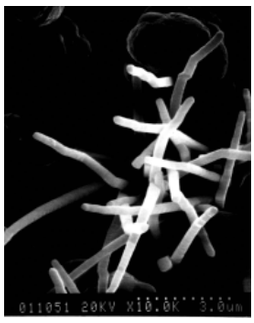

Fig.5 SEM of CVD film [O2] = 25%, 440°C high magnification

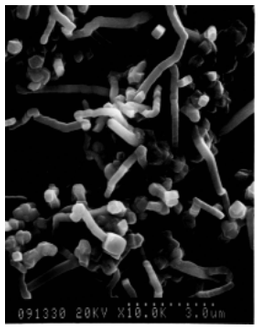

Fig.6 SEM of CVD film O2] = 25%, 400°C low magnification

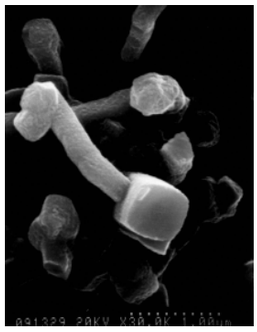

Fig.7 SEM of CVD film [O2]= 25%, 400°C high magnification