A STUDY ON (311) $CuCr_2O_4$
SPINEL FILMS PREPARED BY MOCVD

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Spinel copper chromite, $CuCr_2O_4$, is one of the most effective catalysts for CO oxidation, a key process in automobile-emission control. Previous studies indicated that surface Cu(I) and Cu(0) are the primary active sites, while surrounding Cr_2O_3 phase can prevent Cu(I) and Cu(0) from being oxidized to Cu(II), which will limit the catalytic activity. Through enhancing the decomposition and deflagration rate of ammonium perchlorate/ polystyrene, copper chromite can be used as burning catalyst for solid rocket propellants. The third application of $CuCr_2O_4$ is catalysts for alternative fuels preparations. Copper chromite can be used for synthesizing methanol, an important energy resource for the future, and high alcohol synthesis (HAS), by hydrogenation of CO or CO_2 at 373 K. Recently, $CuCr_2O_4$ is used for reduction of methyl ester, a product form natural abundant coconut and palm kernel oils, to form high alcohol. $CuCr_2O_4$ is commercial available and also used in desulfurization sorbents for hot coal gas in integrated gasification combined cycle (IGCC) power plants.

In this study, we report the first time preparation of copper chromite films by metal organic chemical vapor deposition (MOCVD) with temperature below 500 ^oC. The processing window was: deposition temperature above 420^{o}C, partial pressures of oxygen, above 190 torr, copper acetylacetonate(Cu(acac)$_2$), 0.21 torr, and chromium acetylacetonate (Cr(acac)$_3$), 0.4 torr, respectively. Keeping the more volatile reactants as Cr(acac)3 in excess amount is essential (Fig.1) for depositing stoichiometric films. Higher deposition temperature is essential for depositing oxide films with complex crystalline structure. XRD patterns showed that some $CuCr_2O_4$ films had a preferential orientation at (311) cubic phase, with a lattice spacing near 2.5 Å (Fig.2,3). SEM results showed $CuCr_2O_4$ films exhibited different morphologies such as equiaxed fine grain, truncated polyhedron, and hillocks, depending on the process condition. Both substrate temperature, and precursor partial pressures have significant impact on film morphology and reflect the basic natures of film growth mechanism. XRD patterns indicate that CVD films are polycrystalline, which exhibit highly textured, normal spinel structure (Fig.4, 5). The crystal grain with $d_{spacing}$ = 2.51Å, which is assigned to the (311) orientation of cubic-$CuCr_2O_4$, was frequently observed in XRD patterns. While (211) of tetra-$CuCr_2O_4$ ($d_{standard}$=2.58Å) is another possibility. We also observed $CuCr_2O_4$ grain orientations on (311), (400), and (440) ($d_{spacing}$ = 2.52Å, 2.1 Å, 1.5 Å). CuO (111) phase, with $d_{spacing}$ = 2.32Å, has been foun in some films. At high deposition temperature, one unique feature for XRD results is that $CuCr_2O_4$ phase has a preferential orientation (311) with a broad peak near 2.50 Å. This is suggested that (311) being nucleation favorable. On the growing surface, islands with (311) orientation may have a higher probability to collect migrating adatoms and a higher nucleation rate.

1. Yuneng Chang, Hsinhua Tsen, Mingyung Chen, and Menghsiu Lee,"*A Study on The MOCVD Mechanism of Inverse Spinel Copper Ferrite Thin Films",* 2001 Material Research Society Spring Meeting, symposium U1.9, (2001).

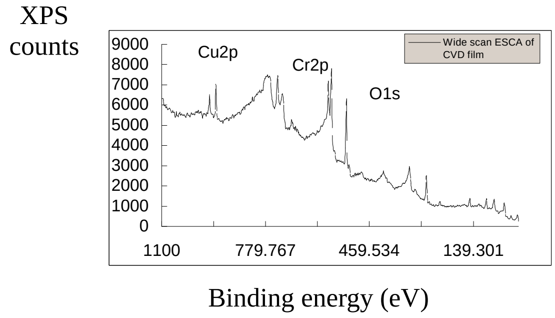


Fig. 1 Survey scan XPS of $CuCr_2O_4$ Film deposited at 380 torr oxygen and 420^{o}C

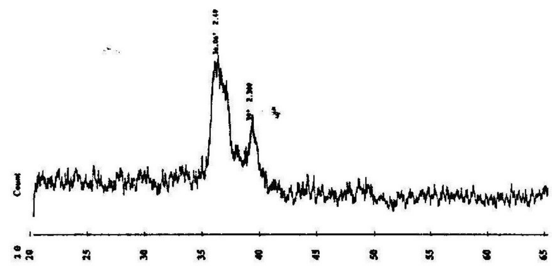


Fig. 2 XRD of $CuCr_2O_4$ Film deposited at 380 torr oxygen and 420^{o}C

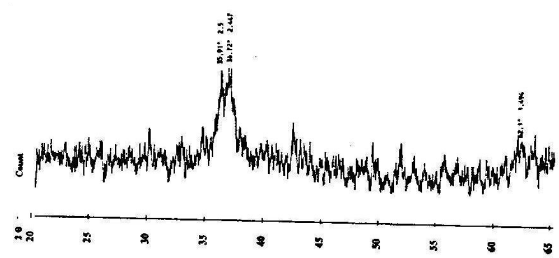
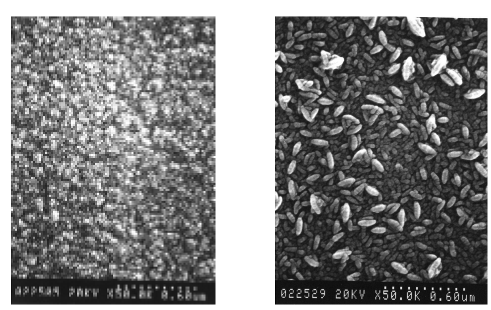
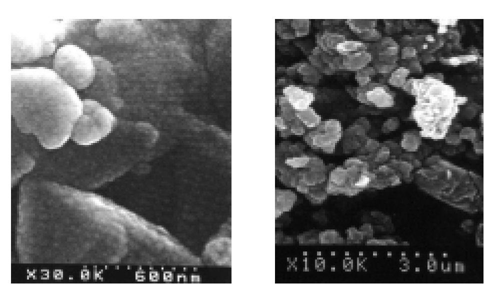


Fig. 3 XRD of $CuCr_2O_4$ Film deposited at 380 torr oxygen and 440^{o}C



(A) (B)

Fig. 4 SEM of $CuCr_2O_4$ Film on Si(100) deposited at 380 torr oxygen and 420^{o}C (A) 440^{o}C (B)



(A) (B)

Fig. 5 SEM of $CuCr_2O_4$ Film deposited at 380 torr oxygen and 420^{o}C, on nonpolished Si(111) (A) and zeolite (B)