POLYCRYSTALLINE SPINEL CHROMITE ($ZnCr_2O_4$) FILMS PREPARED BY MOCVD

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Zinc chromite ($ZnCr_2O_4$) is useful catalysis materials for air pollution control, synthesis of alternative fuel, and sensor materials. A combination set of $Cu_2O/ZnO/Cr_2O_3$ catalyst is extensively used in CO emission control for automobile. With activation energy reduced, the oxide surface accelerate oxidation of CO, at lower temperature (<473 K). XPS an XRD studies show that zinc chromite exist between ZnO phase and Cr_2O_3 phase can stabilize surface zinc active sites and promote conversion efficiency. Interestingly, ZnO is an n-type semiconductor oxide, capable of donating electrons, while Cr_2O_3 is a p-type oxide, capable of extacting electrons. But both are good for hydrogenation catalyst.Recently, Roberts has developed a new process for alcohol synthesis using zinc chromite catalysts for higher alcohol synthesis in a slurry reactor that lead to lower production costs for alternative fuels. In addition to uses in chemical process industry, polycrystalline $ZnCr_2O_4$ ceramic materials, with high porosity and an average grain size of 2-3 μm, applications in moisture sensor through monitoring resistivity changes vs. relative humidity.

In this study, at the first time metal organic chemical vapor deposition (MOCVD) was used to prepare zinc chromite thin films. Metal acetylacetonate precursors $Zn(acac)_2$ and $Cr(acac)_3$ were sublimed at 160°C and 190°C, diluted and transported by N_2/O_2 mixture gas, and deposited chromite films at temperatures above 415°C (fig. 1A, 1B). XRD results indicated that $ZnCr_2O_4$ (220) being the primary phase (Fig. 2, 3). Kinetic studies suggested that increasing oxygen concentration resulted in faster deposition rate, higher film crystallinity, and higher Zn content. A surface reaction model was proposed: on the depositing surface, bonding strength of the more volatile, $Zn(acac)_2$ might be weaker than the less volatile $Cr(acac)_3$. Thus, $Zn(acac)_2$ molecules might occupy less surface sites than $Cr(acac)_3$ molecules did. This limited $ZnCr_2O_4$ film growth rate, while surface adsorbed oxygen atoms can digest released acac ligands to form volatile products such as acetone and CO_2, can also react with Zn adatoms. Increase oxygen partial pressure lead to more $Zn(acac)_2$ adsorbed surface and promoted film deposition. Unlike $CuCr_2O_4$ CVD (Chang, 2001), where $CuCr_2O_4$ phase has a preferential orientation (311), deposited $ZnCr_2O_4$ films are polycrystalline and have multiple grain orientations. Based on JCPDS standards (JCPDS 22-1107), the principle $ZnCr_2O_4$ grain orientations were (311), (220), (422), and (440). Oxygen has a strong impact on film structure. For CVD operated at O_2 free or reduced oxygen concentration, only Cr_2O_3 peaks present in XRD patterns. When O_2 concentration increased, both the deposition rate and number of XRD peaks increased. In this study, we learned that in order to deposit highly dispersed island structure such as catalytic active materials (Fig. 4, 5) , we have to stop the coalescence step in film growth, and to let the discontinuous morphology maintained. The three major coalescence mechanisms, Ostwald ripening, sintering, and cluster migration have to be suppressed. Further, the island size can be managed through control the critical nucleus radius. We might anticipate that by increasing supersaturation ratio in vapor phase, the normal growth rate could be increased.

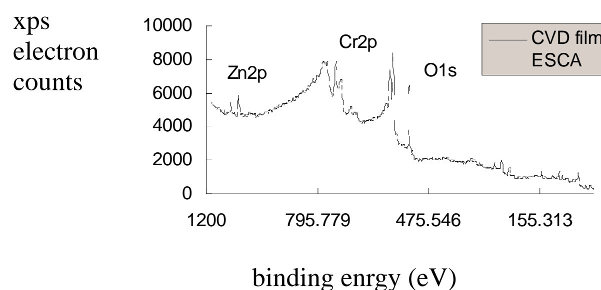


Fig. 1 A Survey scan XPS of $ZnCr_2O_4$ Film at 380 torr of oxygen and 430 °C

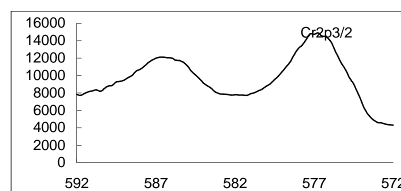


Fig. 1B Detail scan Cr2p XPS of CVD Film at 380 torr of oxygen and 430 °C

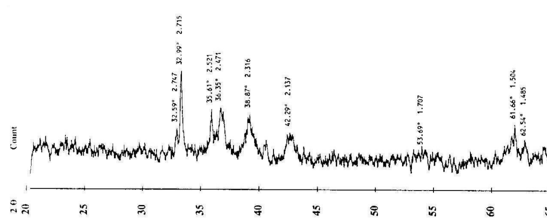


Fig. 2 XRD of $ZnCr_2O_4$ Film at 380 torr of oxygen and 430 °C

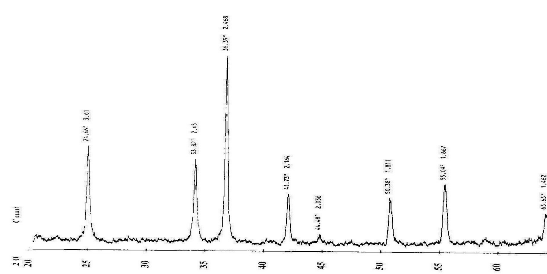
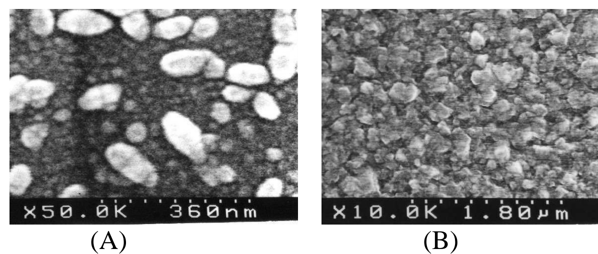
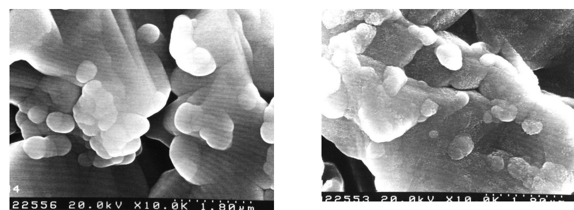


Fig. 3 XRD of $ZnCr_2O_4$ Film at 380 torr of oxygen and 440 °C



(A) (B)

Fig. 4 SEM of $ZnCr_2O_4$ Film on polished Si (100) at 380 torr of oxygen and 420°C (A) 400°C (B)



(A) (B)

Fig. 5 SEM of $ZnCr_2O_4$ Film on nonpolished Si (111) at 380 torr of oxygen and 420°C (A) 400°C (B)