$Cr_3(C,N)_2$ thin films grown by MOCVD as barrier against copper diffusion

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Chromium carbonitride layers were grown by low pressure CVD using $Cr(NEt_2)_4$ as a single source precursor. The depositions were conducted between 380 and 450 °C in a cold-wall vertical reactor.

SEM observations confirmed the highly smooth surface morphology in agreement with the mirror-like and metallic aspect of the layers. Cross-section SEM micrographs showed the good uniformity of the films and a good step coverage of the trenches of various aspect ratios (Fig. 1).

The SIMS analyses revealed the uniform distribution of the elements through the layer thickness.

The resistivity of the films tends to decrease by increasing the thickness. Generally, the thinnest layers exhibit the highest resistivity.

As-deposited films are XRD amorphous. The XRD patterns exhibit a broad hump centered on 20 degrees as shown in Fig. 2. After annealing under H_2 ambient for 30 min up to 650 °C, the only change observed is a splitting of the hump in two broad peaks. After annealing at 700 °C, the films crystallized and the only phase detected is $Cr_3(C_{0.8}N_{0.2})_2$. There is no evidence for interfacial reactions between the CrC_xN_y barrier and the Si or SiO_2 substrate. The resistivity of annealed samples stays equal to 550 µΩ.cm for annealing temperature as high as 650 °C. Then the resistivity drops to 150 µΩ.cm for the sample annealed at 700 °C likely due to the crystallization of the ternary Cr-C-N phase.

The copper films grown by MOCVD on the $Cr_3(C,N)_2$ barrier layers showed an acceptable wettability. Annealing experiments of Cu/ $Cr_3(C_{0.8}N_{0.2})_2$/Si heterostructures were performed in hydrogen ambient for 30 min at various temperatures. Until 700 °C there is no change on the XRD patterns. At this temperature, two phases start to crystallize: $Cr_3(C_{0.8}N_{0.2})_2$ and Cr_2O_3. We assume that the crystallization of Cr_2O_3 originates from the partial oxidation occurred during the growth of the copper film because of the oxygen content of the copper precursor. So the failure temperature of the $Cr_3(C_{0.8}N_{0.2})_2$ barrier is found around 700 °C and the principal degradation process would be the crystallization of the ternary phase $Cr_3(C_{0.8}N_{0.2})_2$.

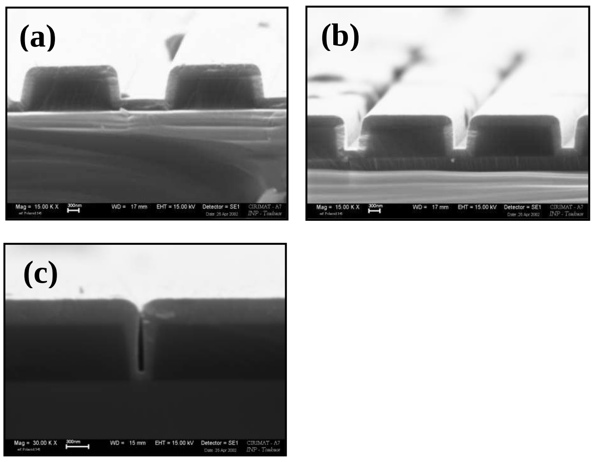

Fig. 1 : Cross-section SEM micrographs of $Cr_3(C_{0.8}N_{0.2})_2$(350nm)/SiO_2/Si heterostructures. The aspect ratios are: (a) 0.38, (b) 0.75 and (c) 1.50.

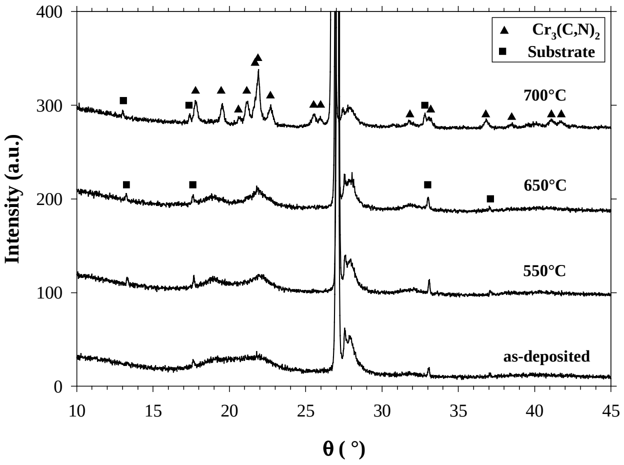

Fig. 2 : XRD patterns of a $Cr_3(C_{0.8}N_{0.2})_2$ (190nm)/SiO_2/Si sample, annealed at various temperature for 30 min in a H_2 ambient.