MOCVD of $CrSi_xC_y$ thin films: study of their potentiality as diffusion barrier

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$CrSi_xC_y$ thin films were grown on different substrates between 400 and 500 ºC using $Cr[CH_2SiMe_3]_4$ as single-source precursor. CVD runs were carried out under 0.5 Torr in a cold-wall vertical reactor using He as carrier gas. Thin films a few tens nanometers thick were deposited with a typical growth rate of 1-2 nm/min.

As-deposited films are XRD amorphous whatever their thickness and the type of substrate are. Annealing of the samples at 700 °C under atmospheric pressure and a H_2 stream for 1 to 15 hours reveals a very stable amorphous structure (figure 1).

The layers have a metallic aspect and a mirror-like surface morphology. The surface roughness is very small ranging from 0.2 to 14 nm for film thicknesses between 30 and 580 nm, respectively. The SEM observations confirm the very smooth surface morphology. Figure 2 shows a typical cross-section of a patterned SiO_2/Si sample coated by a thin $CrSi_xC_y$ layer. The layers exhibit a good step coverage (> 60 %) for trenches with aspect ratios ≤ 1. The SIMS analyses revealed a homogeneous distribution of the main elements up to the interface with the substrate. The figure 3 presents a typical SIMS profiles of a layer deposited on a Ge substrate. Despite the stringent precautions in handling the molecular precursor and during the growth of the films, a very thin oxidized interphase was observed for all samples at the interface with the substrate.

XPS, EDX and SIMS quantitative analyses reveal an increase of the Cr/Si atomic ratio with the deposition temperature. This indicates a decrease of the Si content in the layers due to a better elimination of Si-containing gaseous species derived from the organic ligand CH_2SiMe_3 to the gas phase, while the deposition temperature increases. The most reliable data was obtained by EPMA for a relatively thick film (480 nm) deposited on Ge substrate at 475 °C. For this sample, the Cr/Si ratio is 1.6 that is very similar to the value expected for the only ternary phase of the ternary system: $Cr_5Si_3C_x$ (Cr/Si = 1.67) (1).

The resistivity of as-deposited films decreases by increasing the deposition temperature from 400 to 500 °C to reach typically 100 mΩ.cm at 475 °C. An undesirable oxygen incorporation in the $CrSi_xC_y$ layers (confirmed by XPS, EPMA and SIMS analyses) could explain the relatively high resistivity measured. The XPS analyses reveal that the incorporated oxygen is preferentially bonded to Si (Si 2p at 102 eV) rather than to Cr (Cr 2p3/2 at 574,5 eV).

The excellent thermal stability, high density, amorphous structure, good step coverage of patterned surfaces and the possibility of deposition of nanometric thicknesses make these films as good candidates for diffusion barrier between Cu and Si in electronic devices.

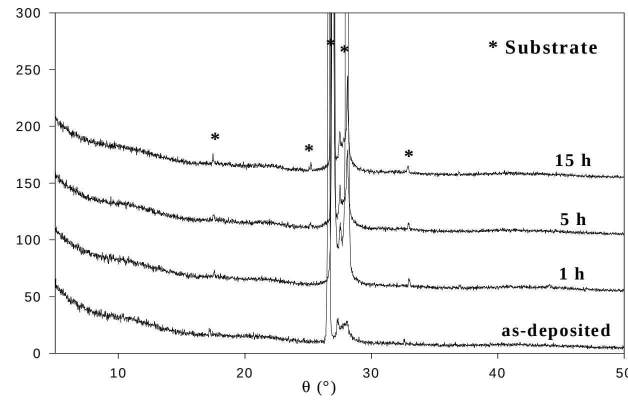

Figure 1: XRD grazing patterns (incidence angle 2 deg) showing the very stable amorphous structure of $CrSi_xC_y$ layer after annealing at 700 °C under atmospheric pressure of H_2 for 1, 5 and 15 hours.

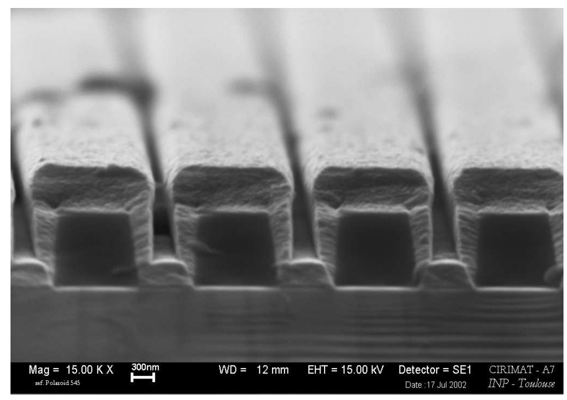

Figure 2: SEM micrographs of a cross section of $CrSi_xC_y$ film deposited on patterned SiO_2/Si substrate showing the high density and good step coverage of the layer

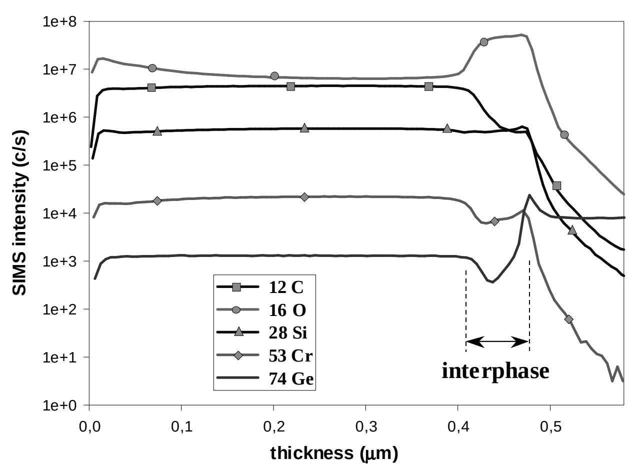

Figure 3: SIMS depth profiles of a $CrSi_xC_y$ film deposited at 475 °C using He as carrier gas on Ge substrate showing a homogeneous distribution of the elements through the film thickness and an oxidized thin interphase at the interface with the substrate.

References

1. Y. Du, J. Schuster and L. Perring, J. Am. Ceram. Soc., **83**, 2067 (2000)