

## CONTRIBUTED PAPERS

# CHARACTERIZATION OF THIN FILMS BY GLANCING INCIDENCE X-RAY DIFFRACTION

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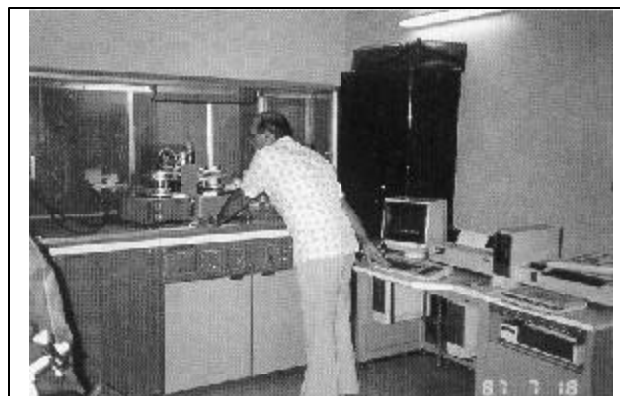
### Introduction

Two dimensional materials created *ab-initio* by the process of condensation of atoms, molecules or ions, called thin films, have unique properties significantly different from the corresponding bulk materials as a result of their physical dimensions, geometry, non-equilibrium microstructure and metallurgy. These characteristic features of thin films can be drastically modified and tailored to obtain the desired properties. This forms the basis of development of a host of active and passive thin films devices [1], in such areas as very large scale integrated (VLSI) circuits, quantum engineering, integrated optics, photovoltaic conversion and special coatings for surface engineering.

The strong relationship of the physical, chemical, metallurgical and electronic structure of thin film micro and nanomaterials with the physical properties of thin materials has led to the development of a large number of microanalytical characterization techniques for thin films. The techniques based on X-ray probe have dominated the field mainly because of their simplicity, more reliability, quantitative and nondestructive nature. Of these techniques, X-ray diffraction has played a leading role, as a fundamental tool for material characterization.

### Experimental Techniques

The conventional Bragg-Brentano (also called  $\theta$ - $2\theta$ ) X-ray diffraction geometry is not useful for the study of ultra thin, graded composition and multi-layered thin films, partly because of poor sensitivity and partly because of the presence of the interfering effect of the substrate. A useful geometry must be based on a low angle of incidence of X-ray, so as to be



able to probe the material up to a specific depth. Three geometries have been exploited for the purpose. The first one is the Seemann-Bohlin parafocusing geometry [2],[3] while the other two are classified in grazing incidence diffraction (GID) and are based on slight modification of conventional Bragg-Brentano geometry. These geometries are discussed in the following.

Fig. 1 shows the Seemann-Bohlin parafocusing geometry. In this geometry the beam focus F, the

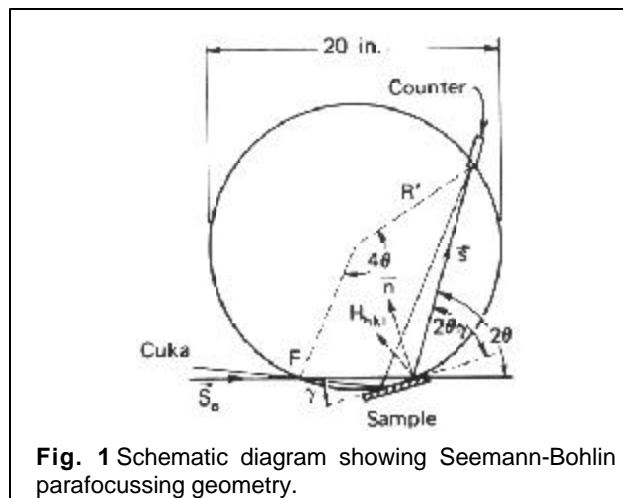
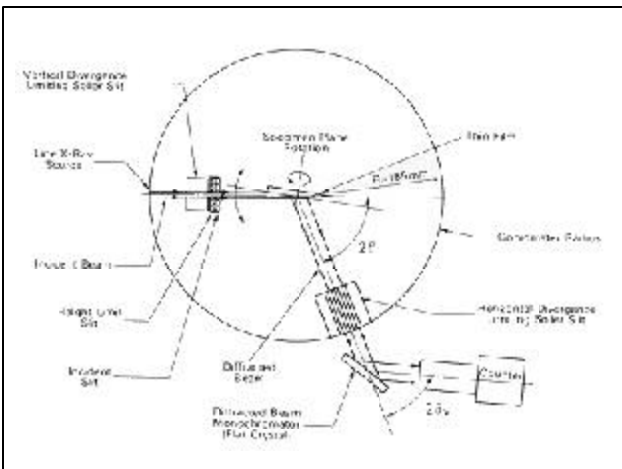


Fig. 1 Schematic diagram showing Seemann-Bohlin parafocusing geometry.

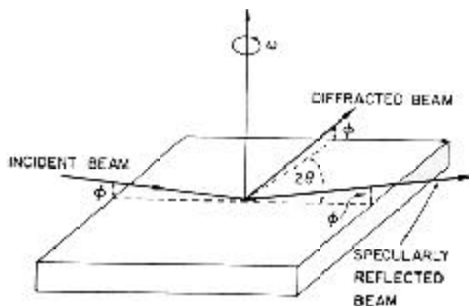
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sample and the counter lies on the same focusing circle. The sample should preferably be curved with radius of curvature of the focusing circle. However, for applications to thin films, the radius of focussing circle is increased considerably in comparison to the sample size. Seemann-Bohlin geometry has certain important advantages for  $\theta \leq 40^\circ$  which includes higher intensity without sacrifice of resolution, simplification of mechanical design and feasibility of employing multiple detectors simultaneously.

One of the glancing incidence diffraction (GID) geometries shown in Fig. 2 is slight modification of conventional Bragg-Brentano geometry. As shown in figure, X-rays pass through a suitable slit system and are made to fall on the sample at a glancing angle ( $\alpha$ ) while the detector on the  $2\theta$  axis scans the XRD pattern. The diffracted beam optics is modified to a parallel beam optics and a flat plate monochromator (graphite) is incorporated in the diffracted beam [4]. The conventional powder methods are applicable in analyzing the GID patterns. One can immediately see the immense potential of this geometry in characteri-



**Fig. 2** Schematic diagram of glancing incidence X-ray diffractometer.



**Fig. 3** Schematic diagram showing glancing incidence X-ray diffraction for epitaxial films.

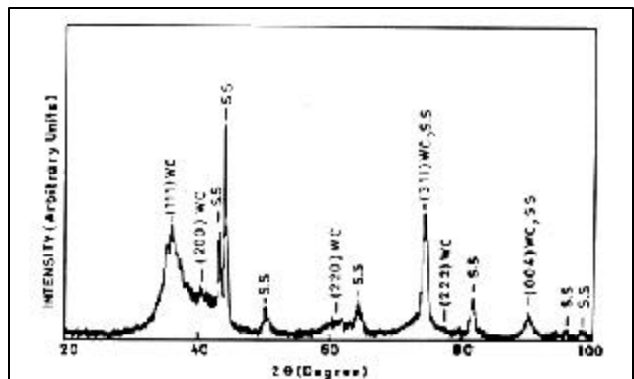
zation of graded and multilayer thin film structures. Fig. 3 shows another GID technique which is capable of analyzing very thin (100 Å) epitaxial layer [5], [6]. As shown, X-ray beam irradiates the sample surface at a grazing angle slightly larger than the critical angle of total reflection. Diffraction is obtained from lattice planes perpendicular to the sample surface. Conventional  $\theta$ - $2\theta$  scan and radial scan provides information about the epitaxial relation, orientational spread, crystallite size and lattice strain.

As can be seen the two GID techniques are complementary in nature and are useful for the analysis of amorphous, polycrystalline and epitaxial thin films.

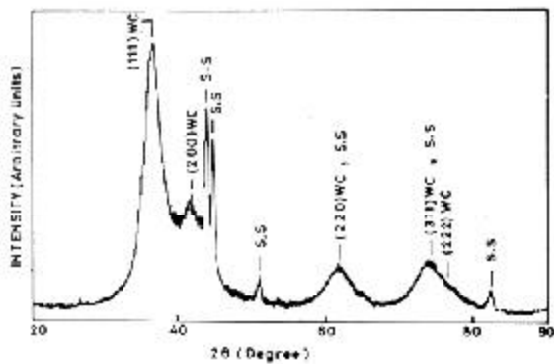
### Experimental Results and Discussion

GID measurements described in this paper were performed in our laboratory on a X-ray diffraction system (Geigerflex D/MAX-RB) from Rigaku Corp., Japan. The system is equipped with a 12 kW rotating anode (CuK $\alpha$ ) source (model RU-200B) and a thin film attachment with sample rotation facility. The schematic diagram is shown in Fig. 2. Thin films of carbides, nitrides, suicides and amorphous chalcogenides were characterized by GID technique. Some of the interesting examples are given below.

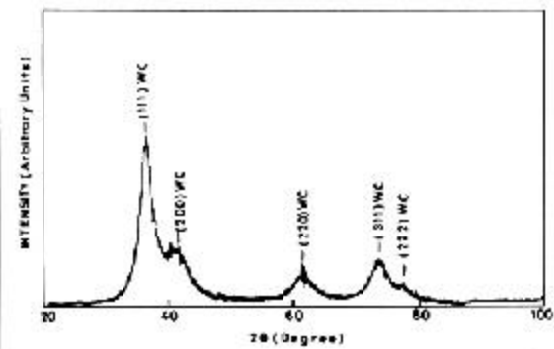
(i) Tungsten carbide (WC)-WC thin films were deposited on stainless steel (SS) substrates at substrate temperature of 500°C by RF reactive magnetron sputtering of tungsten in presence of acetylene [7]. Conventional  $\theta$ - $2\theta$  scan on 8.0  $\mu$ m thick WC film shown in Fig. 4, indicates a fcc B-type structure. The GID scan at  $\alpha=5^\circ$ (Fig. 5) and  $\alpha=2^\circ$  (Fig. 6) indicates that as the angle of incidence is decreased, the peaks corresponding to SS substrate are suppressed. Since no additional peaks other than fcc B-type WC are observed at  $\alpha=2^\circ$ , it can be



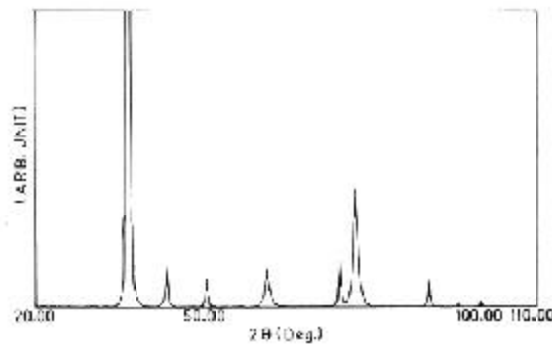
**Fig. 4** Conventional X-ray diffraction pattern of WC films



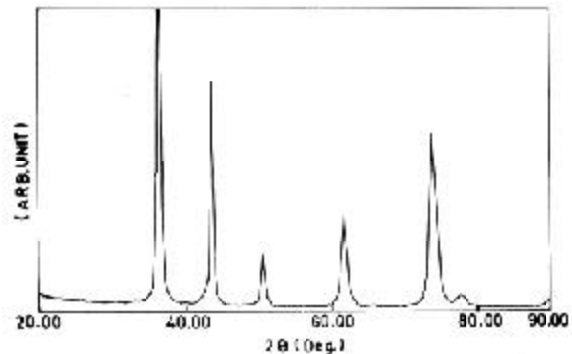
**Fig 5** GID spectra of WC films at an incidence angle  $\alpha=5^\circ$



**Fig 6** GID spectra of WC films at an incidence angle  $\alpha=2^\circ$



**Fig 7** Conventional X-ray pattern for titanium nitride film.



**Fig 8** GID spectra of titanium nitride film at an incidence angle  $\alpha=2^\circ$

inferred that no alloy formation occurred at WC/SS interface.

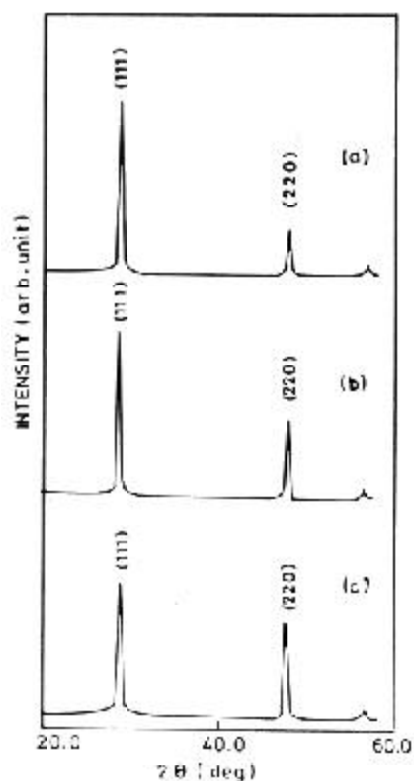
(ii) Titanium nitride-Titanium nitride [8] films on SS substrates were deposited by cathodic arc plasma deposition method in presence of nitrogen atmosphere. Conventional  $\theta$ - $2\theta$  scan and GID scan at  $\alpha=2^\circ$ , respectively, are shown in Fig. 7 and Fig. 8 for a few micron thick film. As can be seen, the intensity of the peaks at  $43.5^\circ$  and  $61.5^\circ$  is enhanced in GID scans in comparison to conventional  $\theta$ - $2\theta$  scan, however the intensity of peak at  $36.3^\circ$  decreases. The enhancement of  $43.5^\circ$  and  $61.5^\circ$  peaks suggests that TiN phase is present at the surface while the bulk of the material is a mixture of TiN and  $Ti_2N$  phases.

(iii) Silicide Films-Refractory metal and near noble metal silicides have become a major area of interest for VLSI metallization and interconnections [9]. The higher density, higher reliability requirements of VLSI technology require closer tolerances on electrical and other properties which also puts stringent demands on coating technology and characterization. Since different phases are formed when metal reacts with silicon, the annealing temperature is an important parameter which decides the formation

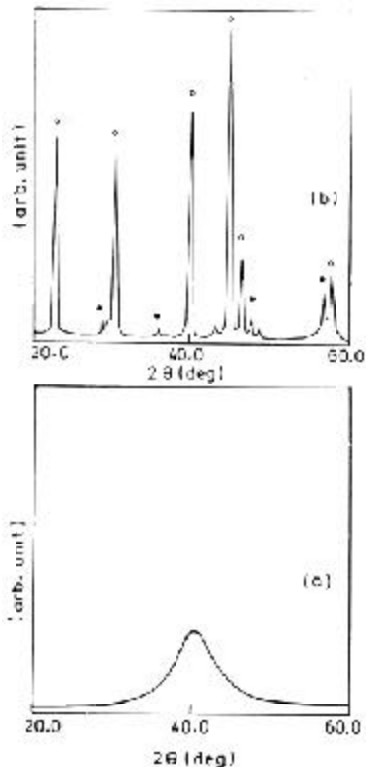
of the final phase. The ion beam mixing and rapid thermal annealing techniques are coming into prominence for their advantages in self aligned silicide (SALICIDE) technology [10]. Also, the interest in multicomponent silicides is obvious if one wants to tailor the properties. All this leads to multicomponent multiphase characterization problem.

Thin films of  $CoSi_2$  in the present study, were formed by rapid thermal annealing of  $500 \text{ \AA}$  of sputter deposited Co film on Si (111) substrates. The annealing temperatures were in  $700^\circ\text{C}$  to  $1000^\circ\text{C}$  range, while the annealing time was 15 seconds. The relative increase in  $CoSi_2$  (111) peak in the GID spectra of Fig. 9 at increasing temperature indicates a preferential  $CoSi_2$  (111) orientation on Si (111).

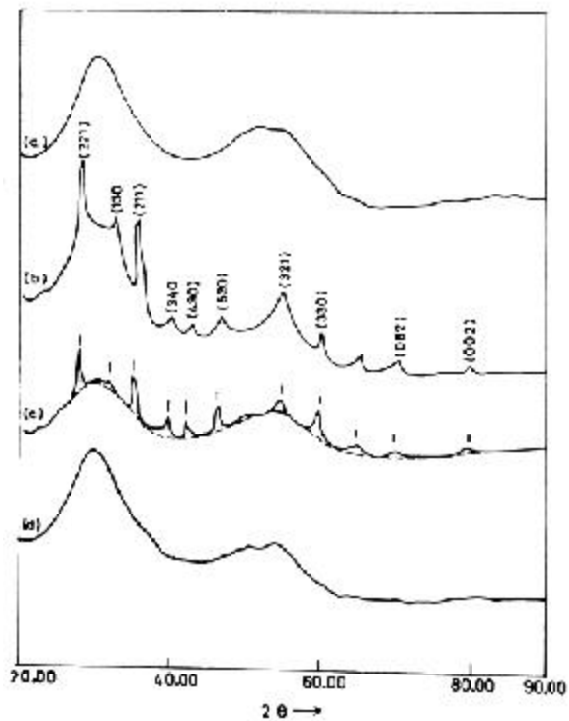
Interaction of amorphous alloys of refractory and near noble metals with Si has been studied by GID technique [11]. Thin films of Mo-Ni alloy were deposited by co-sputtering of Mo and Ni targets on Si (100). The as deposited films are amorphous in nature, Fig. 10(a). The amorphous nature of the films was observed to be stable in the temperature range of  $500$ - $550^\circ\text{C}$  depending upon the composition of Mo and Ni. However, at  $600^\circ\text{C}$ , all compositions leads to



**Fig. 9** GID spectra of 15 sec. Rapid thermal annealed Co/Si (111) samples at annealing temperatures (a) 1000°C (b) 900°C (c) 800°C



**Fig. 10** GID spectra of  $Mo_{67}Ni_{33}$  alloy film on Si (100) at incidence angle  $\alpha=5^\circ$  (a) as deposited (b) after vacuum annealing at 600°C for 30 min.



**Fig. 11** GID spectra for Sb doped Ge-Se films (a) as deposited ( $\alpha=2^\circ$ ) (b) uv exposed ( $\alpha=2^\circ$ ) (c) uv exposed ( $\alpha=5^\circ$ ) and (d) annealed

the phase transformation. The stable phases formed subsequently were identified as  $MoSi_2$  and  $NiSi_2$ , Fig. 10(b).

(iv) Chalcogenide films-Films of Ge-Se, P-Se chalcogenide glasses doped with Ag, Bi and Sb have attracted much attention for their applications as inorganic photoresist [12] and optical memory materials [13]. The amorphous films undergo photostructural changes when exposed to a suitable dose of ultra-violet radiation. Bulk glasses of Ge-Se doped with Sb were first prepared by melt quenching technique. Thin films were subsequently evaporated from the bulk alloy in vacuum of  $10^{-6}$  torr [14]. The GID spectra of as deposited films at an incidence angle ( $\alpha=5^\circ$ ) is shown in Fig. 11 (a). Fig. 11 also shows the GID spectra of the film after suitable ultraviolet exposure at the different angles, Figs. 11 (b) and (c). It is evident from the figure that the film is amorphous before exposure. On exposure,  $Sb_2Se_3$  peaks are observed in GID spectra. The increasing intensity of  $Sb_2Se_3$  peaks at lower angle of incidence indicate formation of polycrystalline  $Sb_2Se_3$  at the surface only. GID spectra at an incidence angle of  $\alpha=5^\circ$ , Fig. 11(c) clearly indicates the superposition of bottom

amorphous matrix on  $\text{Sb}_2\text{Se}_3$  peaks. On annealing the exposed films the  $\text{Sb}_2\text{Se}_3$  peaks disappear as seen in the GID spectra in Fig. 11 (d). These results supported by AES and ESCA studies, suggest evaporation of the ultrathin  $\text{Sb}_2\text{Se}_3$  films.

## Summary

Grazing incidence X-ray diffraction, performed using a thin film attachment and a 12 kW rotating anode source, has been found to be an effective and valuable technique in characterizing a variety of multicomponent and multiphase materials in thin film form. The WC example has clearly ruled out the possibility of alloy formation at WC/SS interface. In the titanium nitride example, conventional XRD only pointed to  $\text{Ti}_2\text{N}$  presence. However, the GID spectra has clearly brought the depth variation in composition of phases. The identification of  $\text{Sb}_2\text{Se}_3$  peaks demonstrates the surface sensitive nature of the GID technique. The silicide study brings out the capability of GID technique in establishing graded multiphase structures in ultra thin films.

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