CHAPTER-III

SYNTHESIS OF COMPOSITE THIN FILMS BY NOVEL HYBRID PULSED LASER DEPOSITION TECHNIQUE.
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SYNTHESIS OF COMPOSITE THIN FILMS BY NOVEL HYBRID PULSED LASER DEPOSITION TECHNIQUE.

III.1 INTRODUCTION.

In recent years, considerable research effort is being spent on developing novel composite-materials so as to meet the need of modern-day technology. These materials include reinforced composites such as cermets, mixtures of oxides and nitrides, metals and polymers etc. The novelty of these materials basically lies in their unconventional structural and compositional state, leading to the possibility of achieving such properties which cannot be realized in the component materials. Considerable advance has been made towards synthesizing these materials in bulk form, however, the area of thin film composites is yet in its infancy. In view of the recent trends of technology which emphasise miniaturization of device features a need is felt to realize these materials in thin film form on a given solid surface. The conventional methods of thin film preparation are not suitable in this context, because these have very limited control on achieving desired micro-structural state of the deposited material. Hence, it is desirable to explore newer approaches to achieve the said objective.

Pulsed laser deposition (PLD), as discussed in chapter I, is one such approach which has definite advantages over other conventional deposition techniques. Although PLD has emerged out as a prime deposition technique, it suffers from a few drawbacks; the major one being generation of cluster and/or particulates. Presence of such objects is of great concern in the context of thin film deposition. A particular type of cluster or particulate can be distinguished from its origin i.e. whether the original matter has been ejected from the target in the solid, liquid or vapor state. Normally the size of the cluster/particulate formed from the vapor state is in nanometer range whereas the dimensions of particulates formed from the solid or liquid state are in micron or submicron range. The shape of the particulate formed from liquid ejecta is normally spherical, while those from solid tend to be irregular. The shape of the particulates from the vapor state can be spherical or polyhedral. Various theories exist regarding particulate formation. Some mechanisms proposed are: (1) mechanical removal of protruding surfaces, craters, microcracks etc. existing on the target surface or being formed during PLD process, (2) rapid expansion and blow-up of the gas bubbles
trapped underneath the target surface as a result of laser irradiation, (3) splashing of the molten layer and (4) condensation from the vapor species due to supersaturation, mostly observed when high background gas pressure is used. By effectively controlling the deposition parameters, one can achieve control over density, size, shape etc. of clusters/particulates, thereby making use of one of the drawbacks of PLD to tailor material properties. Thus a new and exciting field is emerging which utilises hybrid PLD processes to generate novel structures such as composites and nanophase materials possessing exotic properties. In this discussion we shall mainly focus on clusters having dimensions smaller than typical film thickness values and not on macroscopic dust like particles which are ejected due to loose binding and packing. It is important to emphasise that clusters need not always emerge from the target. They can grow on the substrate depending on the growth kinetics and solubility criteria.

I11.2 HYBRID TECHNIQUES.

The search for technologically significant area that could benefit from the unique capabilities of PLD technique led to the birth of a hybrid technique that combined efficiency of Molecular Beam Epitaxy (MBE) with the versatility of PLD. This innovative approach was first demonstrated by Cheung by growing Hg$_{1-x}$Cd$_x$Te band gap tailored material. Fig. III.1 depicts the schematic of the experimental arrangement of this hybrid technique along with other hybrid PLD approaches. The process involved Knudsen effusive cells operated at constant temperature for Hg and tellurium evaporation and a pulsed Nd:YAG laser beam to generate CdTe beam from a high quality polycrystalline CdTe target. This method was also employed to develope compositionally modulated superlattice of Hg$_{1-x}$Cd$_x$Te with gradded barrier and quantum wells.

In order to enhance the energetics of the incident particles from the plasma plume or for creation of an additional plasma discharge in the presence of the background gas, another hybrid technique was developed namely plasma assisted deposition (see Fig. III.1). In this process a biased ring-shaped electrode is introduced in between the target and the substrate. The plasma is initiated by the laser pulse and the continuous discharge conditions can be maintained by proper bias and partial pressure of the background gas. With this approach high quality high T$_c$ YBCO oxide superconductor films have been deposited at substantially lower substrate temperatures. Also, growth of highly crystalline ferroelectric perovskite phase of PZT films has been achieved with this
Fig. III.1  Schematic of hybride deposition techniques.
technique. In a slightly modified process a positive or negative bias voltage is directly applied to the substrate resulting in significant modification in the film properties.

In order to enhance the diamond like carbon (DLC) film properties, a novel plasma hybrid technique was developed. In this ion assisted process the level of plume excitation during PLD was increased by coupling capacitively stored energy to the laser ablated spot in synchronism with the laser pulse (Fig. III.1). Using this technique Krishnaswamy et al. could obtain good quality DLC films over large area. With the help of this technique even hydrogen plasma could be generated to obtain nucleation of diamond particulates.

The PLD process is made to work in synergy with the conventional vacuum arc process to develop another plume excitation process called laser-assisted vacuum arc deposition (laser arc) technique. In this a ring shaped or a planar anode is connected with the target to a pulsed current source. A vacuum arc discharge gets initiated as soon as the laser induced plasma reaches the anode. This technique is used to generate Ti/TiC multilayer films at relatively low substrate temperature.

Injection of electrons into the plasma from an external source, such as, a thermionic filament or a hollow cathode leads us to the development of another technique called as filament assisted PLD process. Here a low-energy electron emitting filament is placed in between the target and the substrate to produce gaseous ions. Leuchtner et al. have adopted this technique to grow PZT films on MgO substrates at relatively lower substrate temperature of 550°C.

The plasma assisted techniques as enumerated above, are easy to adopt and produce films at lower substrate temperatures, but do not always provide adequate control over the characteristics of the ions. In this context a separate source of ions such as a Kaufmann type grid source or an electron cyclotron resonance (ECR) plasma source can provide good control over the ions produced. This has led to the development of ion-beam assisted deposition (IBAD) technique which is schematically represented in Fig. III.1. Use of Kaufmann ion gun has been particularly useful for deposition of high-quality dielectric and optical coatings. Calcium fluoride (CaF$_2$) thin films have been grown on GaAs and Si substrates by using continuous wave (CW) CO$_2$ laser to evaporate CaF$_2$ and Kaufmann gun to ion bombard the growing film. Using this technique very high density films with improved physical and chemical properties are obtained. An important application of this technique is stabilisation of thermodynamically metastable phases which is otherwise impossible to obtain by other conventional methods. This has been seen in reactive deposition of hard c-BN films using KrF excimer laser and Kaufmann nitrogen ion source. There has been lot of impetus in the recent times
to synthesise carbon nitride (C₃N₄) films because of their extreme hardness. The versatility of ion beam assisted PLD process has been effectively used recently to obtain CN films with N/C ratio greater than one. This indicates variety of phase formations closer to C₃N₄, indicating in turn the effective applicability of this process. Oriented Yittria Stabillized Zirconia films on polycrystalline Ni based superalloy substrates have been deposited by Reade et al using PLD with Ar⁺ ion beam at an oblique incidence for the realisation of high Tc YBCO superconducting films.

Instead of the Kaufmann ion source an ECR plasma source can also be used to generate high concentration of atomic and ionic species. There have been number of reports indicating growth of high quality YBCO films using ECR source for generation of O⁺ ions along with copious amount of atomic oxygen. The electron cyclotron source along with application of the magnetic field has proved to enhance the atomic oxygen to ion ratio leading to higher Tc in the YBCO film.

In a novel methodology dual laser beam irradiation of the target surface has been developed to overcome the problem of particulate generation. In this process a laser beam is either split into two beams or two independent lasers with time delay are employed for ablation. This method enables deposition of multicomponent/composite films possessing low dimension particulates. The dual-beam approach is particularly suited as a temporal probe for the study of thin film growth. High Tc superconducting films have been developed using this process wherein two synchronised lasers have been used to ablate YBa₂Cu₃O₇ and CuO targets. This method is important from the stand point of growth of artificially structured multilayer composite coatings.

III.3 EXPERIMENTAL APPROACH

The capability of the PLD technique to interact very effectively with other conventional techniques as seen from the above discussion, set the thought of concurrent use of PLD and conventional thermal evaporation processes to synthesis composite film structures in the present study. The experimental procedure involves collaborative use of pulsed Ruby laser (J.K. Lasers Inc., λ= 6943 Å, pulse width = 30 ns) ablation of the target material and thermal evaporation of another material using tungsten boat as shown in the schematic of Fig. III.2. The evaporants were mounted in a stainless steel vacuum chamber pumped by a diffusion-stack type of vacuum system capable of yielding a background pressure of better than 10⁻⁶ Torr. A quartz lens was used to focus the incident laser beam and in turn to set the proper energy density at the target surface. Since the Ruby laser spot is circular in shape, the energy density was adjusted by variation of the spot diameter. The pulse
Fig. III.2 Schematic of hybrid pulsed laser deposition set-up.
repetition rate was kept at 3 pulses/min which happened to be the maximum available from our laser. During ablation process the laser spot position on the target pellet was changed by rotating it after each pulse. This was done to expose new target surface after every pulse thereby reducing the texturing effects and formation of craters which is inherent to pulsed laser and material interaction process. Simultaneously, thermal evaporation was carried out by resistively heating a tungsten boat so as to achieve a control over the incoming flux. The deposition rate and thereby the thickness of the evaporated material was monitored by using quartz crystal monitor (INFICON XTC, Leybold Heraeus). During the process care was taken to avoid deposition of the evaporant from the tungsten boat onto the target pellet by placing a proper shield. The substrates were mounted on a heater assembly so as to provide sufficient thermal energy for the growth of composite thin films and to increase their adhesion to the substrate. The target to substrate distance was optimised between 3-5 cm. whereas the distance between the tungsten boat and the substrate was kept at a larger distance of about 15 cm. This was done to achieve control over the arrival of the depositing flux. Subsequent to deposition the films were characterised by different techniques like small angle x-ray diffraction (XRD), scanning electron microscopy (SEM), Conversion Electron Mossbauer (CEM) spectroscopy and mechanical hardness tester, in order to get an insight into the nature of the composite character of the films.

III.A PULSED LASER DEPOSITION OF $\alpha$-Fe$_2$O$_3$ CONCURRENTLY WITH THERMAL EVAPORATION OF ALUMINIUM

The simultaneous use of pulsed laser and thermal vaporization process offers an interesting situation, wherein one can get a composite-state defined by presence of clusters of one type of material embedded in a uniform matrix of the other. This concept has been used for the first time, to synthesize Al:Fe$_x$O$_y$ type composites by pulsed laser evaporation from $\alpha$-Fe$_2$O$_3$ concurrently with thermal evaporation of aluminium.

The choice of the matrix in case of metal matrix composites is influenced by its properties such as its ductility, malleability, its interaction with the reinforcing element, thermal and electrical conductivity etc. The current dominant matrix elements are Al and Mg. In the present case Al has been chosen because of the fact that it possesses low melting point (660°C) which enables us to evaporate it by means of conventional techniques. Aluminium is a non-magnetic technology material and hence its interaction with magnetic materials like Fe, iron oxide etc. has generated great interest.
recently. The property of Al to develop a thin oxide layer upon exposure to air makes it an excellent corrosion resistant material and hence has been used in many applications as an oxidation resistant coating. One of the most important oxides of aluminium which is widely used in hybrid electronics technology as a base substrate is Al₂O₃. This compound is also used as an electrical insulator.

Iron oxide has always dominated the field of magnetic materials. This is an n-type semiconducting oxide with anion defects. The crystal structure of α-Fe₂O₃ is that of corundum with closed packed oxygen lattice and Fe³⁺ cations in octahedral sites. This has been shown in Fig. III.3(a and b). The Fig. III.3(a) shows the rhombohedral unit cell and Fig III.3(b) shows the hexagonal unit cell. From both these diagrams it is clear that the Fe cations form the alternate layers along the (111) axis of the rhombohedral cell. It is the most stable oxidation state of iron. Magnetically, it is quiet complex, being antiferromagnetic at low temperature (-10°C) and it undergoes a transition above the Morin temperature to a weak ferrimagnetic state as a result of spin canting, before finally becoming paramagnetic at high temperature. Its unusual magnetic behaviour has been investigated in detail by Mossbauer spectroscopic analysis. The Mossbauer spectrum obtained using a single line source at room temperature comprises of a six line pattern from a hyperfine field of 515 kOe; the chemical isomer shift is +0.38 mm/sec and a small quadrupole interaction of +0.12 mm/sec. Depending on the particle size, there have been several successful attempts of studying superparamagnetic to ferromagnetic transitions in this material by means of Mossbauer spectroscopy. Doping studies on this material by titanium or rhodium impurity shows drastic changes in its Morin transition temperature. Because of its stability in neutral and basic solutions it is used in photocatalytic and photoelectrochemical applications. Although remanant magnetic field or so called 'memory' persists in α-Fe₂O₃ crystals it is very weak in nature and hence this phase of iron oxide does not find great applicablity in magnetic memory devices. The other phase of iron oxide namely γ-Fe₂O₃ or also called as maghemite can hold very high remanant magnetic fields and hence is a natural choice for magnetic tapes and devices.

III.A.1 Experimental.

The experimental approach is as described in the preceding section (see Fig. III.2). The iron-oxide used as a source material for pulsed laser evaporation was 99.99% pure and was sintered in the form of a pellet by normal ceramic processing techniques. Pure aluminium (99.9%, Goodfellow...
Fig. III.3  Schematic of $\alpha$-Fe$_2$O$_3$ structure.
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Metals Ltd., England) was evaporated using the conventional method of resistive heating. The laser energy density of 15 J/cm$^2$ was adjusted at the target surface. The $\alpha$-Fe$_2$O$_3$ pellet was irradiated at a pulse repetition rate of 3 pulses/min. Simultaneously, thermal evaporation of aluminium was carried out from a tungsten boat so as to obtain a deposition rate of 100 Å/min. As indicated in Sec III.2 care was taken to avoid deposition of aluminium on source pellet of $\alpha$-Fe$_2$O$_3$ by using proper shielding. The quartz substrates (1 cm x 1 cm) were mounted on the heater assembly and kept in front of the $\alpha$-Fe$_2$O$_3$ pellet at a distance of 3 cm. The substrate temperature was elevated to about 200°C during deposition. Subsequent to synthesis, the composites were characterized by using Conversion Electron Mossbauer Spectroscopy (CEMS), Small angle X-ray diffraction and Scanning Electron Microscopy (SEM). The use of CEMS technique could facilitate characterization of microstructural state in the composite via knowledge of hyperfine interaction parameters. The CEM-spectra were recorded using constant acceleration type of spectrometer and were computer fitted using the standard MOSFIT code. The small angle X-ray diffraction measurements were performed on Rotaflex RU 200B machine, Rigaku, Japan, while the SEM and EDAX (Energy Dispersive Analysis of X-rays) measurements were performed on Cambridge-Stereoscan 150 system.

III.A.2 Results and Discussion

Fig.III.4 and Fig. III.5 show Mossbauer and small angle X-ray diffraction results, respectively. The Mossbauer spectrum shown in Fig.III.4(a) corresponds to the as-deposited composite. Clearly, the spectrum is of non-magnetic nature and as such can be fitted with a pair of doublets. On the basis of the comparison with the Mossbauer data reported earlier on the Fe-Al-O system one of these doublets having hyperfine parameters viz. I.S. = 1.08 mm/sec, Q.S. = 1.3 mm/sec, can be attributed to the FeAl$_2$O$_4$ phase while the other doublet (I.S. = 0.41 mm/sec, Q.S. = 0.63 mm/sec) to the presence of Fe-Al alloy.

In our earlier studies, we have observed that during pulsed laser evaporation of $\alpha$ Fe$_2$O$_3$ there is a loss of oxygen in going from source pellet to the deposited film leading to the precipitation of non-stoichiometric FeO phase. The absence of Fe-O in the present case clearly indicates that the presence of aluminium in the deposited composite plays an important role in deciding the nature of phase precipitation. Since aluminium has a strong affinity towards oxygen it could strongly react with FeO leading to the precipitation of FeAl$_2$O$_4$ possibly on the surface front of the depositing film itself. The presence of FeAl$_2$O$_4$ phase in the as-deposited composite is also confirmed by small
Fig. III.4  Room temperature CEM-spectra of Al$_2$Fe$_3$O$_4$ composites. (a) as-deposited ; (b) and (c) after annealing at 500°C and 550°C for 1 hour, respectively.
Fig. III.5  Small angle X-ray diffraction patterns of Al₂FeO₃ composites. (a) as deposited and (b) after annealing at 550°C for 1 hour.
angle X-ray diffraction results shown in Fig. III.5(a). If aluminium reacts with FeO to form an Oxygen rich phase like FeAl₂O₄, there should be a precipitation of iron presumably in the form of an Fe-Al alloy. Such an alloy is expected to be aluminium rich leading to non-magnetic contribution in the Mossbauer spectrum. It is well established that the hyperfine parameters in such a case sensitively depend upon local stoichiometry and concentration of aluminium and as such the values of these parameters can vary over a considerably large range. Indeed, we observe such a non-magnetic contribution (the second doublet) in the Mossbauer spectrum of the as-deposited composite. The variation of local stoichiometry of such an alloy is reflected in the broad line width (0.34 mm/s) for this doublet. The presence of such an alloy is also confirmed by X-ray results [Fig.III.5(a)]. In the X-ray diffraction spectrum [Fig.III.5(a)] corresponding to the as-deposited sample, apart from the peaks corresponding to FeAl₂O₄ and Fe-Al alloy phases, there also exists a major contribution corresponding to aluminium. It should be mentioned that the Mossbauer data can give only iron related information while the X-ray data give information about all the participating structures.

Our earlier studies revealed that approximately 10 Å³ equivalent of material is deposited per pulse in laser evaporation of α-Fe₂O₃ at an energy density of 15-20 J/cm²; while the rate of deposition of aluminium was 100 Å°/min. The state of composite is thus expected to consist of finely dispersed clusters of laser evaporated iron-related material in aluminium matrix. The SEM results shown in Fig.III.6(a) confirm this proposition. It is interesting to note that the shape of clusters is of doughnut-type [Fig III.6(b)]. Associated with each cluster there is a shadow region underneath where aluminium flux could not reach due to its directionality. It should also be noted that the doughnut shaped appearance of the cluster might have resulted due to the morphological effect. If we consider that spherical-shaped clusters are primarily deposited, then at the end of the synthesis process, the topmost clusters would receive aluminium-flux selectively over central area. This situation would render doughnut shaped appearance in SEM-photograph. If, however, some of the clusters are truly doughnut shaped, it could mean that these clusters are frozen matter from a liquid state which has picked up rotational momentum from the surface currents during ablation. The EDAX measurements carried out on a typical cluster revealed that the concentration of iron varies over the cluster dimension, being minimum at central region, increasing towards the outer part, and decreasing again near the outer-edge region of the cluster. We could not detect aluminium concentration by EDAX because of detector sensitivity problem.
Fig. III.6 SEM picture of as deposited Al:Fe$_x$O$_y$ composite showing distributed clusters of iron related material.
When the as-deposited composite was vacuum annealed at 400°C for 1 hour, the state of composite was undisturbed as revealed by Mossbauer measurements. However, after annealing at 500°C for 1 hour, Mossbauer measurements [shown in Fig. III.4(b)] revealed initiation of phase transformation. The Mossbauer spectrum of such a sample shows a small amount of magnetic contribution of a sextet (IMF 330 kOe) representing precipitation of α-Fe. The corresponding X-ray spectrum (not shown here), however, could not reveal such a precipitation probably because of its small amount in the total material.

We annealed the sample at 550°C for 1 hour to accelerate the process of phase transformation. The corresponding Mossbauer spectrum is shown in Fig. III.4(c). When this spectrum is compared with that shown in Fig. III.4(b), it is clear that further phase transformation has taken place. The magnetic contribution is substantially increased at the expense of non-magnetic phases. The magnetic contribution is composed of two sextets, one corresponding to α-Fe phase (I.M.F. value 330 kOe) and another to non-stoichiometric iron rich Fe-Al alloy (I.M.F. value 212 kOe). It is established that h.f. field at Fe\(^{57}\) nucleus decreases progressively at a rate of 26 KOe per aluminium neighbour\(^{43,46}\). Thus the latter sextet (IMF value 212 KOe) can be attributed to a random Fe-Al alloy in which Fe\(^{57}\) atom have an average of four aluminium neighbours. The non-magnetic part consists of two doublets. One doublet corresponds to Fe-Al alloy phase as discussed earlier while the other doublet (I.S. = 0.07 mm/sec, Q.S. = 0.66 mm/sec) corresponds to Fe\(^{3+}\) in disordered aluminium Oxide\(^{47}\). The contribution of these non-magnetic phases however is much smaller as compared to magnetic phases. These results clearly indicate that thermal annealing results in dissociation of FeAl\(_2\)O\(_2\) phase leading to precipitation of α-Fe and iron rich Fe-Al alloy. The liberated oxygen can subsequently react with aluminium to form aluminium oxide which can not be seen by CEMS technique. However, the XRD data [Fig. III.5(b)] can and do show formation of AlO phase in the sample.

III.B SYNTHESIS OF COMPOSITE THIN FILMS OF WC PARTICULATES DISPERSED IN Al MATRIX.

Having proved the potential of concurrent PLD and thermal evaporation process for synthesis of composite microstructure, an attempt was made to extend this idea for synthesis of Al:WC\(_{1-x}\) composite. The inclusion of a hard component like tungsten carbide in the matrix of Al can help in strengthening the matrix thereby increasing its hardness.
Tungsten carbide is one of the prominent members of the group VI transition metal carbides which has received wide attention recently. It is well known for its high melting point, hardness and good corrosion resistance. The industrial use of this material in its bulk form as a cutting tool is well established but its applicability as a hard coating is being explored recently. These films are found to have good diffusion barrier properties and have applicability as X-ray mirrors. Tungsten carbide films have been prepared by number of techniques like chemical vapor deposition (CVD), DC arc plasma, rf magnetron sputtering, and dc sputter deposition. The films deposited by rf magnetron sputtering technique on stainless steel substrate are found to possess high hardness (3200 kgf/mm²) and good adhesion. The role of interfacial buffer layer of materials like Ti, Ta, Mo etc. have also been studied to understand their effect on the structure and mechanical properties of WC coatings. Still very little efforts have been made towards synthesis of these films for their surface mechanical applications. It has been found that the synthesis of these films is a complex process due to the existence of lower carbide phases.

III.B.1 Experimental.

The target used for the laser ablation was 99.95% pure WC pellet (Sandvik Asia, Ltd.) and for evaporation pure aluminium (99.9 %, Goodfellow metals Ltd., England) was used. The experimental procedure employed was the same as described in III.3. The laser energy density was maintained at 30 J/cm² at the target surface giving a deposition rate of about 2 Å/pulse. Corning (7059) substrates were used in these experiments. The samples in the form of strips (1cm x 1cm) were cleaned by standard chemical processing procedure. They were rinsed in methanol and cleaned in the ultrasonic bath to remove contamination of dust particles. these substrates were mounted in front of the target on a heater. The composite layer of Al:WC was deposited by the same process of concurrent deposition technique as demonstrated in the previous case. During composite deposition the Al evaporation rate was maintained at ~ 0.3 Å/sec and was monitored by the crystal monitor. The film thickness measurement was carried out by using standard Talystep instrument (Rank Taylor Hobson) and the final composite layer was estimated to be ~ 5000 Å thick. Subsequent to deposition the films were characterised by small angle x-ray diffraction technique for its structural characteristics and the morphology was examined by scanning electron microscopy. For XRD measurements the grazing angle of incidence was kept at 0.5° in order to obtain structural
III.B.2 Results and Discussion

Fig. III.7(a) shows the low angle XRD pattern of the as prepared pellet of WC. The spectrum clearly indicates presence of well defined diffraction lines. The intensity ratios and the line positions are well in agreement with those reported for the powder samples consisting of the polycrystalline WC phase. The XRD pattern corresponding to tungsten carbide film deposited on the corning substrate having thickness of 1500 Å is shown in Fig. III.7(b). The spectrum was recorded at an angle of incidence of $\alpha = 0.5^\circ$. This value is slightly smaller than that of the critical angle of x-rays having wavelength of 1.5406 Å, in tungsten carbide material. Thus, below the critical angle, the penetration depth is expected to be only upto few hundreds of angstroms there by giving the structural information from only the film. By increasing the x-ray incidence angle to $\alpha = 1^\circ$ a broad hump centered around $2\theta = 25^\circ$ is observed relating to the substrate peak. This leads us to conclude that the information obtained is from the film only. There is a considerable difference between XRD pattern corresponding to the source WC pellet and that of the deposited film. The XRD pattern of the pellet shows sharp lines at $2\theta$ equal to 37.2°, 42.6°, 43.4°, 49.6°, 62.8°, and 74.9°. They indicate formation of predominantly WC$_{1-x}$ along with W$_2$C phase. The tungsten carbide film deposited on the corning substrate (Fig. III.7(b)) from this target, shows a broad hump which is characteristic of WC$_{1-x}$ phase. Previous studies carried out by our group $^{56,57}$ on deposition of WC using an unreacted pellet of W and C indicates that whatever be the state of starting material, the end result of PLD process is stoichiometric film formation. This has been clearly indicated by the XRD pattern in Fig. III.7(b). Thus, stoichiometry of the source pellet has been maintained although, the structure of the material could not be maintained. The presence of small peaks overriding above the broad hump indicate presence of WC and W$_2$C microcrystallites. However their contribution is much smaller as compared to the amorphous phase in the film. The amorphous nature of the film indicates the disorder in the film. Fig. III.7(c) shows the grazing angle x-ray pattern of the composite microstructure of Al:WC film on corning substrate. As indicated above the XRD patterns were taken at an incidence angle of 0.5° so as obtain the structural information from the deposited layer. The XRD pattern clearly indicates a broad peak with a doublet pattern. The peak at $2\theta = 38.5^\circ$ belongs to Al (111) phase along with a peak at $2\theta = 40.2^\circ$ belonging to W$_2$C phase and also present is the WC$_{1-x}$.
Fig. III.7  Small angle X-ray diffraction patterns of (a) as prepared bulk WC target, (b) WC film on Corning (7059) substrate, and (c) Al:WC composite film on Corning (7059) substrate.
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phase at $\theta = 36.5^\circ$. Thus the composite film contains mixed phases of WC along with the appearance of Al peak. This gives us the indication of the possibility of dispersion of WC clusters in Al matrix. The Al during deposition seems to have reacted with the ablated WC particulates giving rise to appearance of WAI and AIC type of phases. In order to minimise the segregation of these phases deposition was carried out at low substrate temperature of 100$^\circ$C. In order to explore the possibility of enhancement in the crystallinity of the film, attempts were made to deposite the films at higher substrate teperatures. Also other process parameters were varied to a slight extent. But the substrate temperature could not be raised beyond 300$^\circ$C since it led to softening of the Al matrix leading to wrinkled films with occasional peeling off. Also, the XRD paterns for the films deposited at higher temperatures did not show much variation with the hump remaining broader in nature.

Thus, the process parameters certainly influence the composite film growth. The hardness measurements were carried out on the composite film of about 5000 Å thickness. The smaller film thickness obviously influences the microhardness measurements leading to a relative hardness data. Due to this reason the measurements were carried out at a low load of 10 gm. Different sample regions were subjected to indentation. The composite film showed a variation in the hardness value with maximum of 561 HV. This value is comparable with that of only WC film which is equal to 520 HV. The variation in hardness in the composite film indicates that the hard WC clusters get embedded in the Al matrix during the concurrent deposition process. Since, the pulse repetition rate of the Ruby laser is only 3 pulses/min, there is a lot of time inbetween the two pulses for different phases to precipitate, which has been clearly revealed by the XRD pattern. One of the disadvantages of the low repetition rate in this case is that the deposition rate cannot be increased further, leading to lower cluster density in the film. Still the hardness value of these composite films is much higher as compared to only Al films which is areound 33 HV only. In order to understand the effect of higher loads, indentation tests were carried out at 50 gm. loads. It was observed that cracks developed near the indentation mark. Upon close observation it was seen that these cracks did not propogate along the film implying that they must have got terminated at a point where another WC cluster is present.

In order to understand the surface morphology of the composite films, scanning electron microscopy was carried out. Fig. III.8 reveals the microstructural details of the film at two different magniificaations. The lower magnification picture taken at 2.8Kx reveals highly woven Al matrix with WC clusters embedded in it. The cluster size seems to vary between few hundred angstroms to more than a micron, which supports our observation of variation in hardness value at different locations on
Fig. III 8 SEM picture of as deposited Al:WC composite film at different magnifications.
the film surface. At higher magnification of 8Kx the film morphology reveals crater formations which might have been created due to the impingement of high velocity laser ablated WC clusters. Also, there is a presence of variety of clusters with different cluster dimensions. Some of larger clusters reveal characteristic features. They seem to possess a characteristic doughnut shape which was also observed in the case of Al:Fe$_2$O$_3$ composite films. This might be arising again due to the inherent nature of the concurrent deposition process wherein the clusters can be considered to be frozen matter from a liquid state which has picked up rotational momentum from the surface currents during ablation. Thus, the SEM picture clearly shows that WC clusters have indeed got embedded into the Al matrix.

III.4 CONCLUSION.

The concept of simultaneous use of pulsed laser evaporation and thermal evaporation is used for the first time to explore the possibility of synthesis of composite materials in thin film form. It is demonstrated that appropriate control on process parameters can indeed lead to realization of a composite film wherein clusters of laser deposited material are embedded in a continuum matrix of the thermally evaporated material. In the case of Al:Fe$_2$O$_3$ system, the Mossbauer studies along with XRD analysis reveal formation of FeAl$_2$O$_4$ phase along with Fe-Al alloy phases. Thus the state of the composite consists of finely dispersed clusters of laser evaporated iron-related material in Al matrix. Thermal annealing studies of these films show that there is dissociation of FeAl$_2$O$_4$ phase into $\alpha$-Fe and Fe-Al alloy with AlO phase.

Application of this technique also allows synthesis of composite structures such as Al:WC composite coatings. In this case, the hardness of the Al matrix has been improved by the inclusion of the dispersed WC clusters. Also, the presence of these clusters in the soft Al matrix helps in arresting the crack propagation in the film.
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41. This MOSFIT programme was originally written by E.Kreber from University des Saarlandes Saarbruken and it was adoped for ICL 1904S computer by S.K.Date, National Chemical Laboratory, Pune, India.