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The 1995 Distinguished
Materials Scientist Lecture

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My experiments with thin films—the nanostate of matter*

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Born in 1933 at Chahal Kalan, Panjab (now Pakistan), Kasturi Lal Chopra experienced along with his family the fiery turbulance of partition to reach Delhi. After topping in the matric examination from DAV School in 1948, he went on to earn his B. Sc. (Hons.) in 1952, and M. Sc. (1954) in Physics from Delhi University. As a World University Service Fellow, he took his Ph. D in Low Temperature Physics from the University of British Columbia, Canada. After being a post doctoral fellow at Royal Military College of Canada, and Max Planck Guest Scientist at the Fritz Haber Institute, Berlin, he took up the assignments of a Group Leader at Philco-Food Scientific Laboratory. Blue Bell in 1962 and later a Staff Scientist of Ledgemont Laboratory, Kennecott Copper Corp., USA. The IIT Delhi invited him in 1970 as a Senior Professor to head the Physics Department and establish a school of Solid State Physics. He founded the Thin Film Laboratory and served IIT Delhi for 17 years in various capacities as Head, Physics Department, Energy Centre, and Dean, Post Graduate Studies and Industrial Research and Development. He was appointed Director of IIT Kharagpur in 1987 and is presently serving a second term. He continues to actively pursue R/D activities along with research students and faculty in the Thin Film Laboratory in IIT Delhi, as also in the Microscience Laboratory founded by him at IIT Kharagpur. He has supervised over 60 Ph. D Theses, published over 400 papers and authored/coauthored: "Thin Film Solar Cells", "Thin Film Phenomena", "Thin Film Device Applications", and has edited four other books. Several published papers are now Classic Citations and "Thin Film Phenomena" continues for the last 25 years to be considered a "Bible" of the field. Innovative developments of Prof. Chopra and colleagues have resulted in five US Patents, a dozen knowhow transfers to industry in India and abroad. He has served on the editorial boards of several international journals. He has lectured extensively abroad in various universities and R/D centres

and consulted to several international companies. He has been elected a Fellow of the American Physical Society, Indian National Science Academy, Indian Academy of Sciences and Indian Academy of Engineering. He has delivered several memorial lectures and is the recipient of several awards: Bhatnagar Prize (Physics), Bhatnagar Award (Energy), FICCI Award (Science & Technology), Bhasin Award (Energy), Bhabha Award (Applied Sciences), INSA Krishnan Memorial Lecture Award.

Abstract. The black art of thin films exhibiting whimsical properties and thus called 'the fourth state of matter' enticed the author to a challenge to unravel the mysteries of matter created *ab-initio* on a nanoscale. Nucleation and growth studies of evaporated and sputtered films (both polycrystalline and epitaxial) and the effects of kinetic energy, angle of incidence, electric field, substrate agitation, formation of metastable and amorphous structures, etc led to exciting discoveries. The fields of amorphous metal alloy and semiconducting films were thus born. Electron and optical transport investigations on pure and doped metal, semiconducting, oxide and polymer films established a variety of new phenomena of which the mean free path effects and specular scattering of conduction electrons in epitaxial metal films, giant thermopower in quenched metal films, sputter quenching, giant photocontraction effect in amorphous Ge-chalcogenide films, enhancement of superconducting transition temperature in transition metal films, nanosize multi layer coating (the first known superlattices) are noteworthy. A variety of new deposition processes such as solution growth of polymer films, solution growth of chalcogenide and oxide films, spray pyrolysis, coprecipitation of multicomponent oxides (for thick films), activated reactive evaporation/magnetron sputtering were innovated. This lecture will share the excitement of the contributions by the author, his 60 Ph.D students and a number of post doctoral fellows and faculty members at the Thin Film Laboratory, IIT Delhi and the Microscience Laboratory at IIT Kharagpur.

Keywords. Thin films; nanostate of matter; amorphous semiconductors.

1. Prologue

I am grateful to MRSI for the honour done to me. I consider this honour as a tribute to the devoted efforts of my 60 Ph.D students and a number of faculty colleagues, working together harmoniously. Whatever little I have achieved in developing and furthering the field of science and technology of thin films—the nanostate of matter—I owe it in a large measure to the support of my coworkers as a big family.

I started my research career over four decades ago trying to unravel the mysterious quantum dynamical properties of superfluid helium films of nanometric size below 1°K. Little did I know then that I will spend the next thirtyfive years of my active life studying atomistically created matter in the form of thin films of micro and nano size dimensions. Today, I have chosen to present before you a broad survey of many milestones which my coworkers and I have established in the field for the last three decades. Needless to say that it is a personalized account of my scientific career and thus I have taken liberties in presenting the highlights in an informal way.

I entered the field purely by an accident. A scientist of the Philco Scientific Laboratory, USA developed in 1960 an all thin-film metal-insulator-semiconductor active device which enthused the company so much that a new R/D laboratory was established to exploit this invention. The invention was short lived for lack of good understanding of electron transport processes in thin films of metals and insulators but its impact in opening new frontiers was enormous. Recruitment of scientists/engineers took place all over the world and I was hired while attending a scientific meeting in Brussels.

On taking up my position in USA, my job was to understand the basic electron transport properties of metal films—at a time when these films were considered the '*fourth state of matter*' in view of their temperamental properties and behaviour depending on who deposited the films and how and where.

2. Electron transport properties of metal films

As the film thickness becomes comparable to the mean free path of conduction electrons (typically, a few hundred Angstroms or less at 300 K) in metal films, the surface scattering (also called mean free path or size effects) becomes a dominant process controlling resistivity. A simple Fuchs–Sondheimer theory had given us guidelines of what we should expect in cases of diffuse/specular scattering of electrons. Nobody had ever tried to observe specular or even partly specular scattering, simply because one required an atomically smooth electron mirror surface for which deposition technology had to be improved. Using a simple dc diode sputtering process (a novel technique at that time), I succeeded in obtaining atomically smooth epitaxial gold films on single crystal mica substrates. And, lo and behold, I observed reasonably high specular scattering—which means a resistivity close to the bulk value was obtained down to very small thicknesses, as illustrated in figure 1. The results, first of its kind, were published in *J. Appl. Phys.* and were well received. In fact, this paper (a classic citation) started a gold rush of publications on size effects in various electron transport properties of metal films for the next two decades.

Elated with the success, I extended my investigations to tunneling studies in thin-film sandwich structures of M_1–I–M_2 type, using valve metals with their controlled

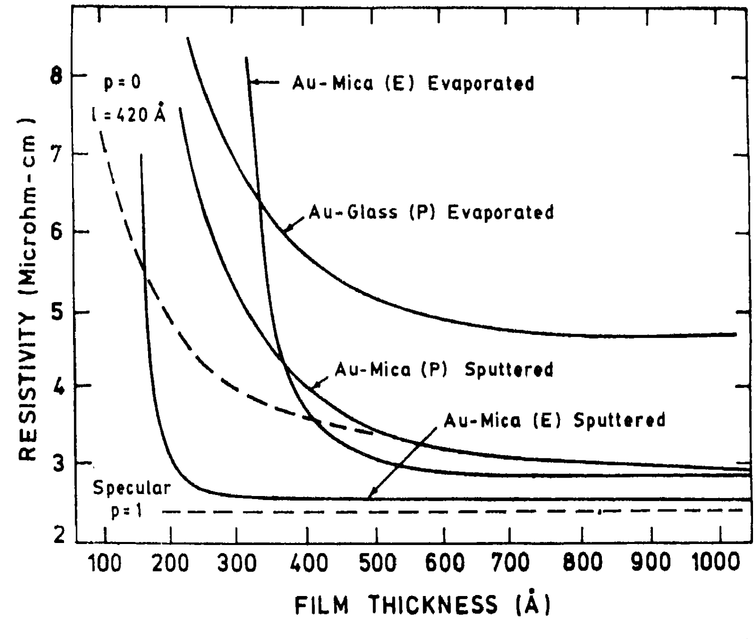

Figure 1. Thickness dependence of the electrical resistivity of evaporated (E) and sputtered (SP) polycrystalline (P) and epitaxial (EP) gold films deposited on mica and glass. Also shown (broken line) is the theoretical (Fuchs–Sondheimer theory) variation for diffuse and specular scattering of conduction electrons.

thickness of the oxide film. Whereas virgin structures showed rectifying behaviour with tunneling characteristics, a 'forming' (essentially high current density shock) process yielded current-controlled negative resistance (CCNR) and a switching behaviour from a high resistance to a low resistance state as illustrated in figure 2. This

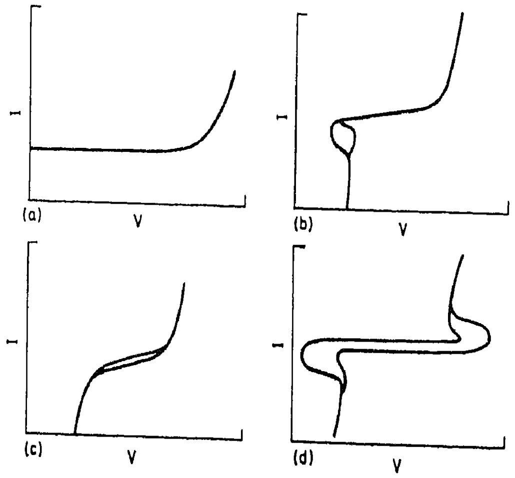

Figure 2. Schematic current – voltage characteristics of Nb–Nb oxide–Nb thin film sandwich structure as it changes from virgin state (a) through (c) on successively increasing voltage leading to 'forming', switching and current controlled negative resistance behaviour.

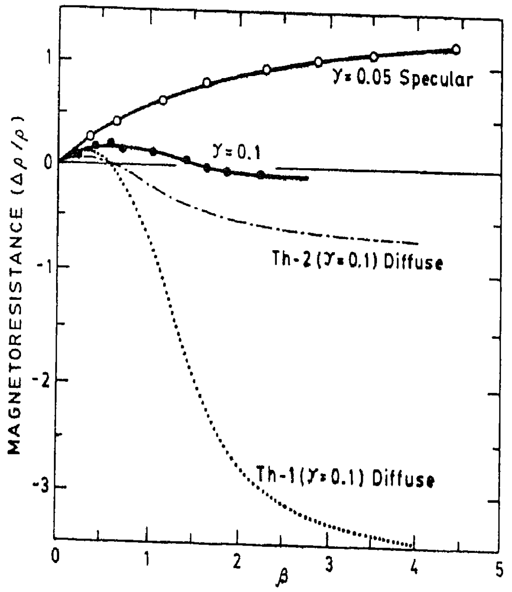

Figure 3. Longitudinal magnetoresistance at 4·2°K as a function of $\beta = t/r$ (t, film thickness and r, Larmor radius) for epitaxial (111) Ag/mica film (○○○) and polycrystalline Ag/mica film (■■■). Also shown are theoretical variations for diffuse scattering normalized with respect to bulk (Th–1) and thin film (Th–2) resistivity for $r = t/l = 0{\cdot}1$ (l = mfp of conduction electrons).

behaviour is very similar to that exhibited by two back-to-back glass discharge tubes. This discovery had all the elements of an exciting drama in view of its possible applications. A switching and a negative resistance behaviour in amorphous chalcogenide glasses was published formally (it was already known in trade journals) in *Phys. Rev. Lett.* by Stanford Ovshinsky. This most advertised paper with US newspapers headlining a possible Nobel Prize for Ovshinsky for revolutionizing electronics became a major centre of controversy and it involved reference to our results. As we know now, switching in MIM structures involving a whole range of insulators and high resistivity amorphous/glassy materials is a ubiquitous phenomenon. But, its long term stability and reproducibility are not good enough for large scale electronic applications.

In view of the importance of the mean free path (mfp) effects on electron transport properties to solid state physics, as also the science and device applications of micro and nano materials, we continued investigations on such parameters as temperature coefficient of resistivity, Hall coefficient, magneto-resistance, thermopower, thermal conductivity of well-behaved ultra thin metal and alloy films. The work was done partly at the newly created Ledgemount Laboratory of Kennecott Copper Corp. of USA (which I joined in 1964) and later in the Thin Film Laboratory which I established from scratch after I joined the Physics Department of IIT, Delhi on August 23, 1970. Basically, the purpose of these studies was to identify quantitatively the role of various scattering processes prevailing in polycrystalline and epitaxial metal films. The observed existence of a size effect in the Hall coefficient was a surprise. At temperatures down to 4·2 K, and high (~ 100 kG) magnetic fields, the scattering effects can be enhanced (by increased mfp), or reduced (by having Larmor radius comparable or smaller than the film thickness). The result of such studies done at the National Magnet Laboratory, Boston are shown dramatically in figure 3 for diffuse and specular scattering case of silver films.

Inherent in the process of *ab-initio* creation of matter by a random atomistic condensation/deposition process with limited adatom mobility is the possibility of

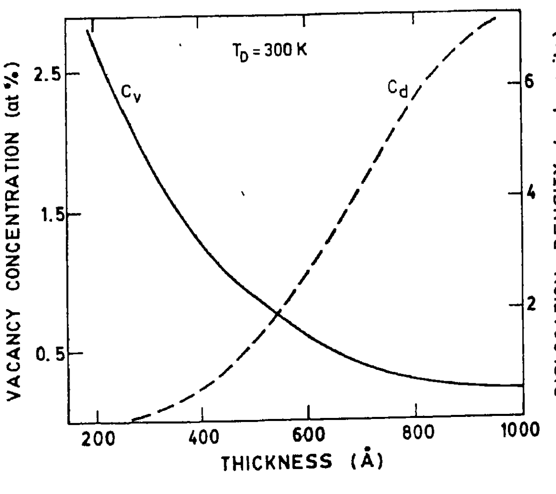

Figure 4. Schematic thickness variation of vacancy and dislocation concentration in vapour quenched copper films deposited at room temperature.

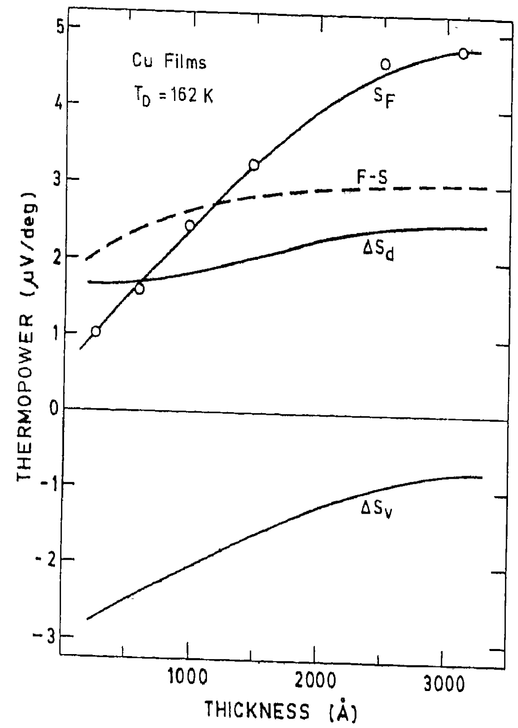

Figure 5. Thickness variation of thermopower (S_F) of copper films deposited at 162°K. Also shown are derived vacancy (ΔS_v), dislocation (ΔS_d), and theoretical (F–S) contributions.

creation of a range of point, line and planar defects in very large nonequilibrium concentrations. By condensing thermally created vapours on substrates at low temperatures (vapour quenching), or by condensing energetic sputtered (vapour) species in a sputtering process (named 'sputter-quenching' by us), one may vary the type and concentration of defects over a large range, as shown in figure 4. Our systematic studies have established the contribution of the defects in various scattering processes. An interesting example of how effective the vacancies and dislocations are in determining the large thermopower observed in quenched copper films is shown in figure 5. It is to be noted that the contributions are opposite in sign indicating the dependence of the curvature of the distortion of the Fermi surface on the type of defects.

Co-deposition of two or more metals under appropriate conditions results in a highly disordered and even amorphous structure. This is particularly true of sputter-deposition process. And, thus, this process has been utilized by us to prepare various amorphous alloy films. As the films become amorphous, the resistivity rises very rapidly by almost two orders of magnitude. A good example is shown in figure 6 for the case of Cu–Ag films. We interpreted these effects in Cu–Ag and Cu–Ni films as due to localization of electrons. This was proposed at a time (1966) when localization was being debated hotly. Our proposal was not appreciated by many, including Neville Mott at that time. Now, of course, localization of electrons in metallic glasses is widely accepted.

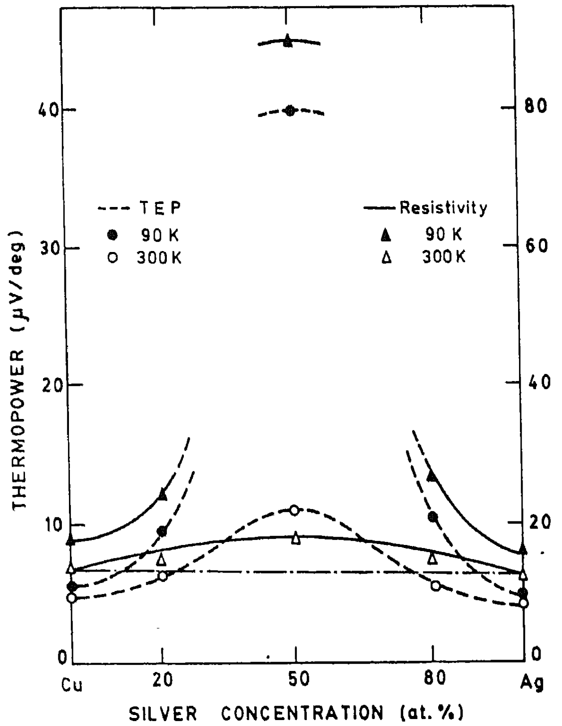

Figure 6. Resistivity and thermopower variations as a function of Ag concentration in Cu–Ag films vapour quenched at 90 and 300 K. As the films became amorphous around 50% concentration, transport parameters rose very rapidly.

3. Nucleation and growth of films

The pioneers in the field recognized very early the importance of the role of nucleation and growth in determining the structural behaviour and properties of thin films. Thus, in the late 50's and early 60's, tremendous R/D effort was made to study the early growth stages with electron microscopy techniques, using *in situ* and *ex situ* techniques. Our studies yielded remarkable results and several new and interesting phenomena/effects which in summary are:

(i) Nucleation density determines the critical thickness at which film continuity takes place.
(ii) Nucleation density is affected by the kinetic energy of the vapour species and its angle of deposition.
(iii) Nucleation density can be enhanced considerably by suitable physical and chemical changes on the surface.
(iv) Epitaxial growth takes place at the nucleation stage although the final epitaxial relation may change during growth.
(v) Kinetic energy of sputtered species can be utilized effectively to obtain epitaxial growth of some metal films at temperature as low as 77 K.
(vi) Ultrasonic agitation of the substrate enhances adatom mobility and consequent oriented growth.

(vii) Application of an electric field in the plane of a growing island-like field enhances coalescence of the discrete islands as a result of induced attractive coulombic forces between two charged islands of different sizes, or very small separation.

(viii) By using suitable deposition conditions, in particular controlled vapour and sputter-quenching, a whole range of metastable structures can be stabilized at the nucleation stage. Our studies led to the enunciation of several empirical rules for the occurrence of metastable structures in thin films. These rules include: (a) Wurtzite structure materials can be deposited in sphalerite form and *vice versa*; (b) sputtered bcc and hcp transition metals can be stabilized to assume fcc structures; (c) slightly distorted NaCl crystal structures get undistorted, and (d) CsCl structure halides assume abnormal NaCl structures.

While searching for new methods to stabilize metastable structures, an ion beam deposition was developed for the first time, using a modified duoplasmatron source so that the deposited films nucleate and grow under controlled conditions without a direct exposure to the plasma. One of the major applications of ion beam depositions is

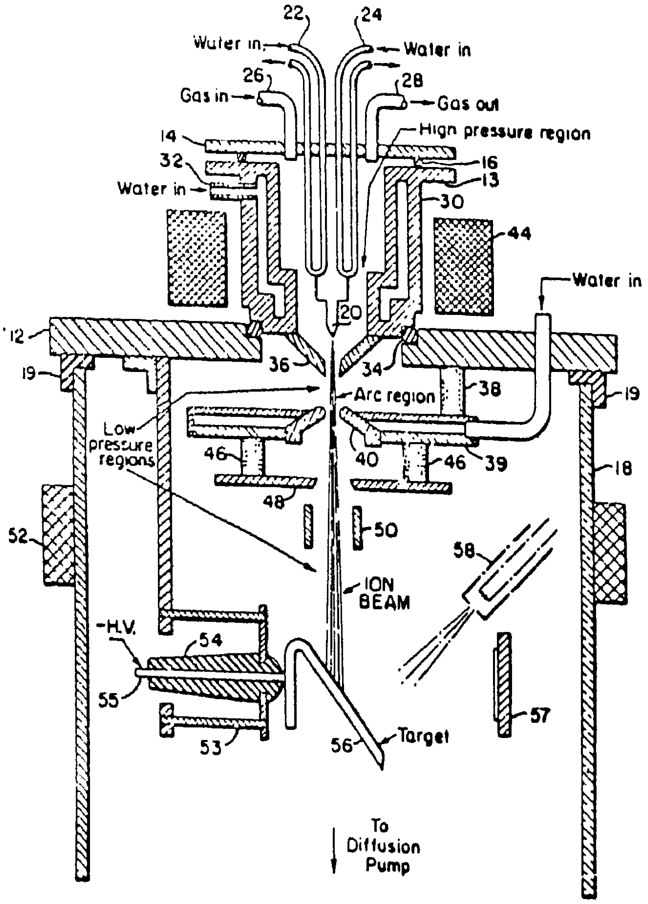

Figure 7. A schematic diagram of a high current duoplasmatron source for ion beam deposition (US) Patent 3, 409, 529 dated Nov. 5, 1968 granted to Chopra and Rendlett). The numbered components are described in the patent.

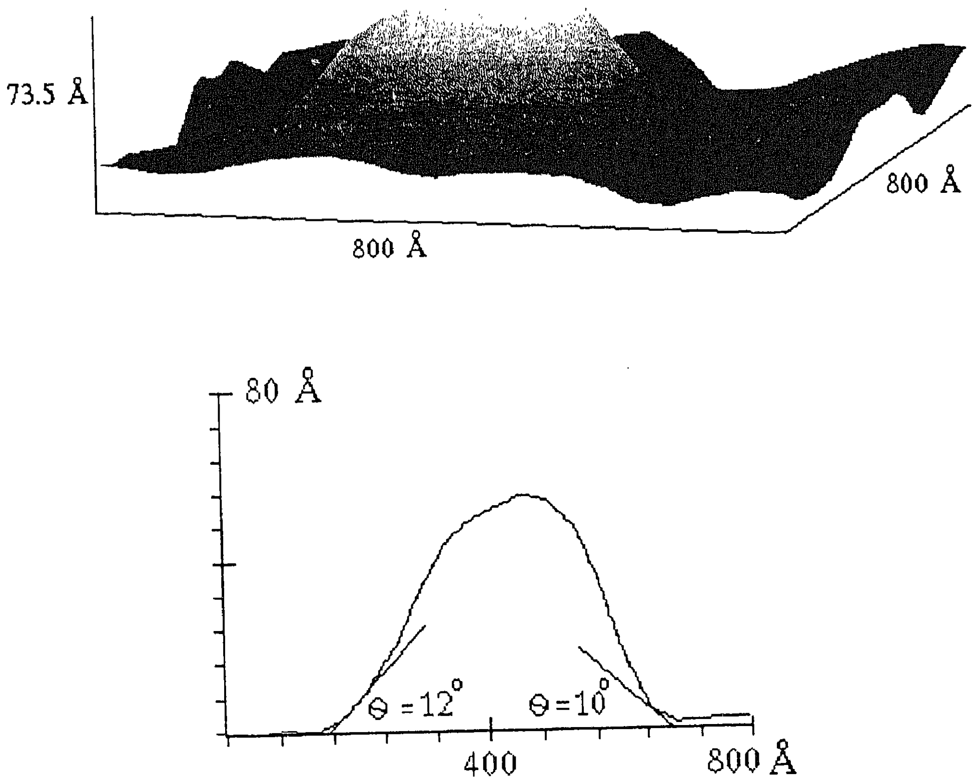

Figure 8. STM image of a single island in a thin (~ 20 A) silver films deposited on gold coated mica substrate at room temperature (top). Also shown is a line profile across the island to determine the angle of contact (bottom).

preparing high quality, strongly adherent transition metal and other optical coatings for laser mirrors and laser gyroscopes. A major (1·2 billion dollar) legal suit filed by Litton Industries against Honeywell on the patent rights for a suitable ion beam technology for laser gyroscope mirrors has been decided in favour of Honeywell drawing heavily for evidence on the very first US patent No. 3,409,529, issued to us on November 5, 1968 for our duoplasmatron source shown in figure 7. It should be pointed out that, at present, more versatile ion beam sources based on different ion extraction principles are available commercially and are being used extensively in R/D institutions and industry.

With the availability of a very powerful new tool of scanning tunneling microscope (STM) in the late eighties, we have once again taken up recently the study of nucleation and growth of films in our newly created Microscience Laboratory at IIT, Kharagpur. STM allows a very convenient atomic resolution three dimensional imaging of nanostructures such as the earliest nucleation stage of films. Figure 8 shows an STM micrograph of a metal island. For the first time, it has become possible to measure directly the contact angles—a critical parameter in nucleation theories. As we had surmised over two decades ago, the contact angle between a substrate and self-deposit is rarely zero for nanostructures. This explains why a three dimensional hemispherical growth rather than a two dimensional growth is the most common mode of growth of

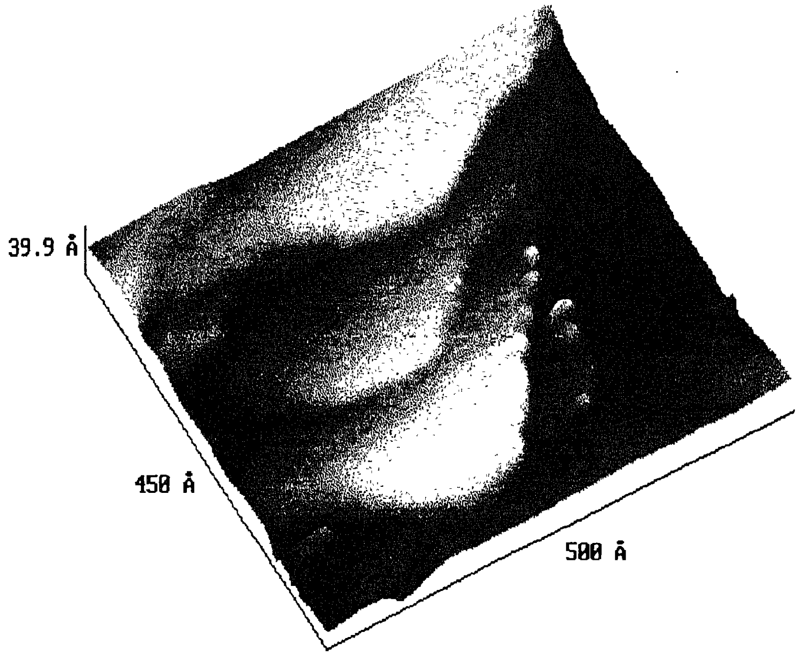

Figure 9. STM micrograph of an epitaxial sputtered YBCO/MgO film showing layered growth pattern.

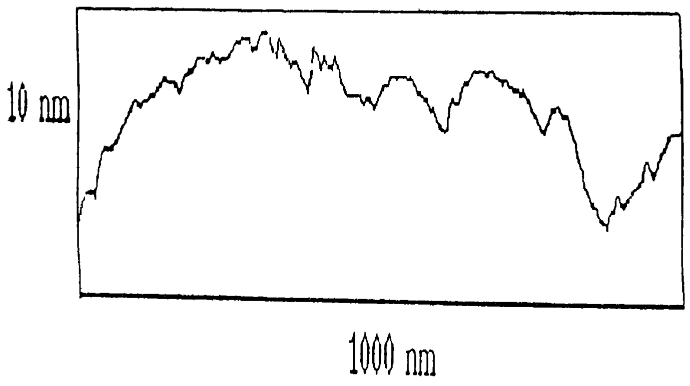

Figure 10. Surface roughness profile of an epitaxial YBCO film sputter deposited on MgO as determined by a scanning tunneling microscope.

films. The STM allows observations of microscopic defects such as vacancy clusters, line defects, spiral growth, etc. Excellent example of layered (and spiral growth) characteristic of sputtered films of high T_c Y-Ba-Cu-O superconductor, is shown in figure 9. Such studies have allowed us to synergetically vary plasma deposition conditions to obtain very smooth (rms roughness ~ 10 nm) Y-Ba-Cu-O/MgO films as shown by an STM profile of figure 10.

Recently, we have exploited the high field between the top of the STM probe and the metal films to create nanosize hills and valleys. While we are in the process of understanding these new phenomena, it is clear that STM has provided us a powerful tool to modify surfaces and to generate lithographic and reprographic patterns on a nanoscale with obvious applications in nanotechnologies/nanoelectronics.

4. Amorphous semiconductors

In order to look for quantum size effects in a bismuth-like material, an assignment was given to a Ph D student (S K Bahl) to study GeTe films since this slightly distorted rhombohedral structured degenerate semiconductor (band gap ~ 0·4 eV) has properties very similar to Bi. However, to our surprise, the evaporated films of GeTe were found to exhibit nearly ideal intrinsic semiconductor behaviour with a very sharp well-defined optical gap of 0·8 eV. Further studies led to conclusion that vacuum evaporated films on room temperature substrates were ideally amorphous with a sharp (~ 1 K) transition from amorphous to crystalline phase (both metastable fcc and the stable rhombohedral), attended by over six orders of magnitude change in electrical resistivity. It is the only known amorphous semiconductor in which the local short range order changes drastically on going from crystalline to amorphous state. When these results were announced in an American Physical Society meeting, the IBM group led by Leo Esaki was taken by surprise since the group had made similar observations but had not published. Our GeTe results attracted the attention of Neville Mott who explained our results on the basis of simple calculations that we were dealing with the case when the mfp is comparable to atomic dimension and Anderson localization has set in.

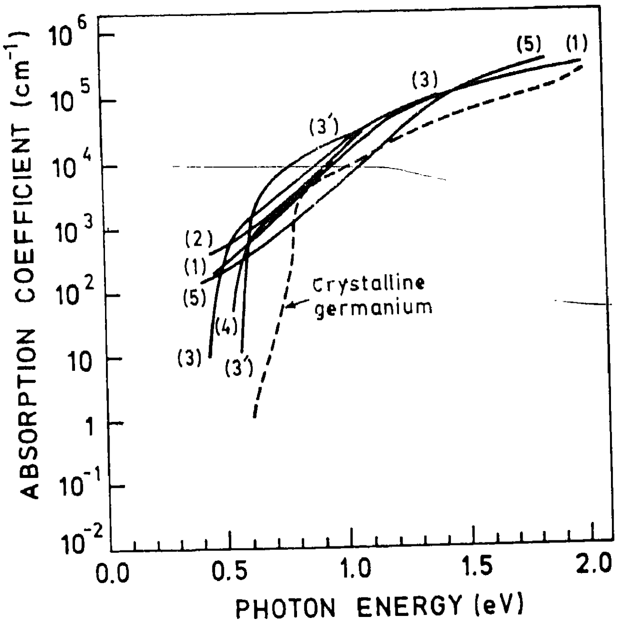

Figure 11. Optical absorption coefficient vs photon energy near the absorption edge of amorphous Ge films as reported by several workers: (Clark 1967; Chittak 1970; Spicer and Donovan 1970; Tauc 1970; Chopra and Bahl 1971). The broken curve for crystalline Ge is from Dash and Newman (1955).

As we investigated GeTe films around 1966, amorphous semiconductors, in particular chalcogenide glasses which exhibited well defined optical gap and intrinsic semiconductor-like behaviour, became a hot subject. Being simpler, elemental semiconductor films of Ge and Si (which are amorphous if deposited at or around room temperature) attracted world wide attention for revealing the mystery of prevailing short range and long range order and its impact on the properties which are conventionally understood on the basis of translational symmetry. Amorphous (a-) Ge films defied simple understanding. The films showed reasonably sharp optical absorption edge which shifted considerably to energies lower than that of crystalline (c-) Ge. However, both the slope and shift depended on how the films were deposited and how the optical absorption was measured. A typical example of this sensitivity is shown in figure 11. It was clear that although a-Ge films exhibited the same short range order as c-Ge, the long range order was different and it depended on deposition conditions. As an example, the density of a-Ge films could be varied anywhere up to 40% lower than that of c-Ge.

An ideally amorphous structure can be created only by random condensation of atomic species with zero adatom mobility. On the other hand, a finite adatom mobility is required in order to establish a well-defined short range order, particularly in a tetrahedrally coordinated amorphous semiconductor such as Ge and Si. The existence of a finite adatom mobility in vacuum evaporated, a-Ge film was beautifully demonstrated by us by observing nucleation decoration patterns (figure 12) on a NaCl substrate having such defects as ledges and dislocations. Nucleation studies have established that adatoms move to nucleate preferentially on defect sites to form critical nuclei. The large separation between nuclei is a measure of the large adatom mobility which has been enhanced by using a clever technique, pioneered by us, of oblique deposition of Ge vapours.

Structural, electrical, optical and thermal properties of a-Ge films could be varied over a wide range by using the oblique deposition technique which provides controlled porosity at a microscopic level in columnar structured films. Variation of the several properties was found to follow a universal behaviour as shown in figure 13. Exhaustive studies by our research group on a-Ge allowed one of the earliest verifications of various theoretical concepts (e.g. localization, mobility gap and variable range hopping conduction) proposed to explain electron transport behaviour of amorphous semiconductors.

It was a natural extension of our studies to add metallic doping/alloying impurities to a-Ge. We were the first to report that porous a-Ge films could retain very high (up to 40 at%) concentration of various metals (e.g. Ge, Au, Fe, Ni, etc) without destroying the tetrahedral structure of the amorphous films. On the basis of our structural studies, we called these as a-Ge-metal alloy films. As expected, the addition of alloying metals affected drastically the hopping conduction and the slope of the optical absorption edge. These results were explained in terms of modifications of the band structure of a-Ge films. Alloying in some case also converted *p*-type behaviour of a-Ge to *n*-type. While visiting Prof. W Spear in Dundee, Scotland, I talked about these results to him and Marc Boodsky who was also visiting at that time. I was then made aware of their successful efforts in 'doping' a-Si films to convert from *p* to *n*-type. This is, of course, a historic discovery which opened a vast new field of a-Si:H films for electronic and photo-electronic applications. And, naturally, our research group was there in the field.

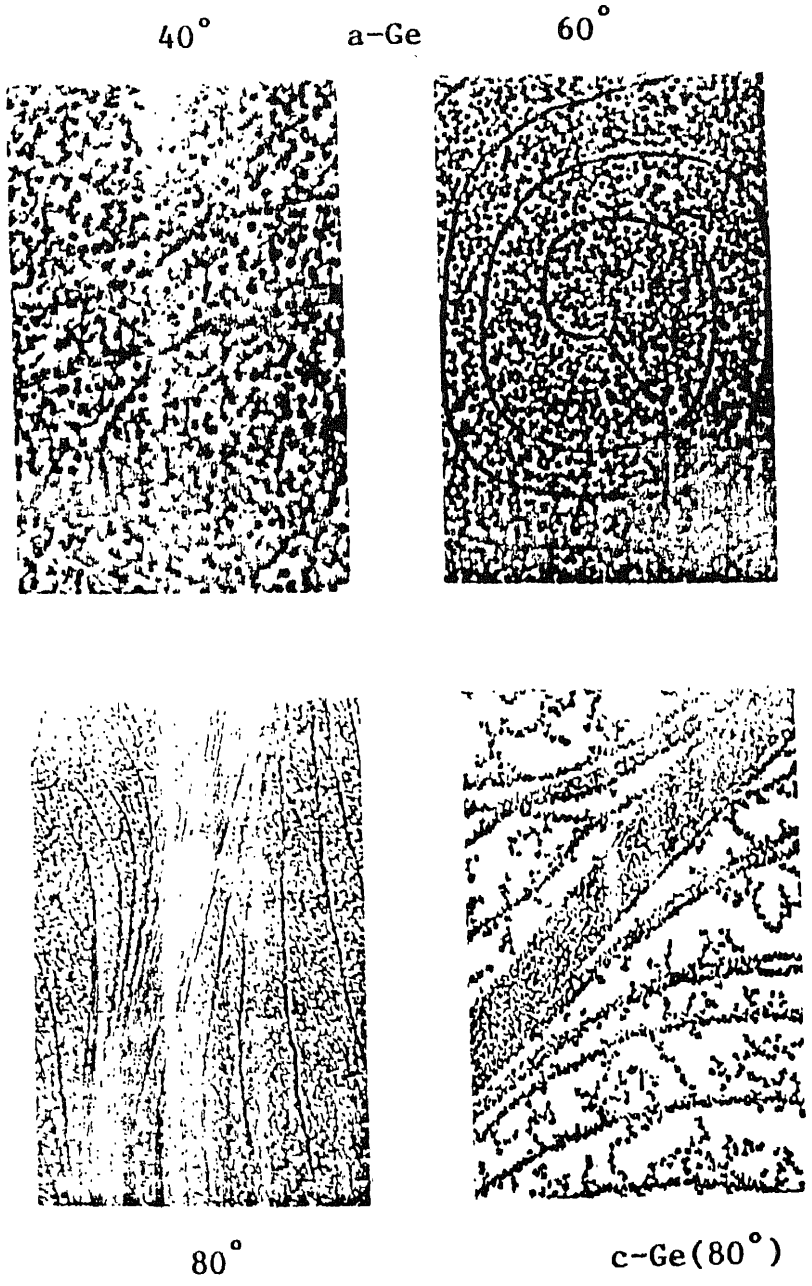

Figure 12. Nucleation decoration patterns obtained by oblique (40, 60 and 80 degrees) deposition of 100A a-Ge film at 200°C on NaCl having surface defects of ledges and spiral dislocations. Also shown is the high adatom mobility decoration pattern for obliquely (80°) deposited C-Ge film.

Several Russian and Japanese scientists had reported small (1%) photo-induced reversible and irreversible structural and optical changes in such chalcogenide glasses as As_2S_3 and As_2Se_3. The role of chalcogen and its electronic structure (the lone pair electrons) appeared to be the key parameter. We posed ourselves a question: How can

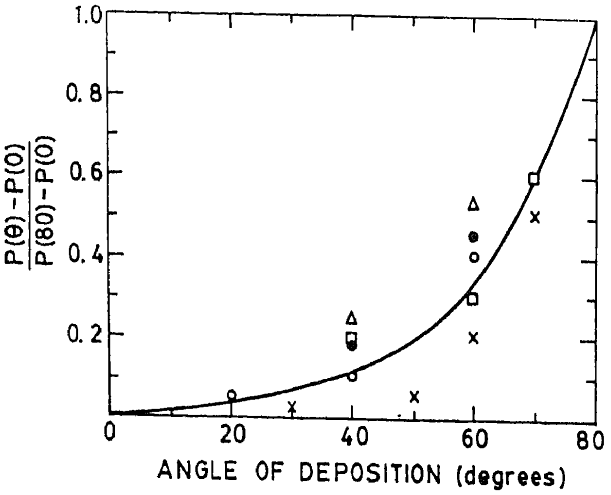

Figure 13. Variation of normalized properties (P) of a-Ge films with angle (θ) of deposition. $\theta = 0$ for normal incidence. Properties are: resistivity (×); refractive index (Δ); optical absorption edge (○); density (●); and crystallization temperature (□).

we enhance the photostructural effects? A possible way was to provide structurally unstable a-Ge as the matrix for a chalcogen to exhibit large photoeffect. By depositing (thermally) a-GeSe$_{1-x}$ films at oblique angles of incidence, we made the startling discovery that the films simply collapsed on suitable illumination. The films were densified physically as much as 12%. A concomitant change in the refractive index by ~4% and a small shift (increase) in the optical absorption edge were observed. Our excited research group undertook a lot of work to explain the origin of the effect. We established that such an effect is not observed in a-Ge but only in a-Ge based alloys/compounds with S and Se and also other chalcogenide glasses such as p-Se. The higher the porosity of the thin film, the larger the effect was. The existence of columnar structure and its collapse on illumination was established by electron microscopy techniques. This was later neatly verified by small angle neutron scattering studies. It was concluded that physical densification resulted from the collapse of columns which, in turn, led to optical densification. Further, as a result of these changes, chemical dissolution, metallic diffusion (e.g. that of Ag) and electrochemical deposition of metals onto these films were modified drastically. Consequently, it became possible to produce lithographic, reprographic and metal coating patterns on the surface of thin film with excellent resolution down to submicron dimensions. This opened a new frontier of the use of inorganic materials for wet and dry microlithography.

Since it was such an unusual and unexpected effect, which we named as 'giant photocontraction', there was a natural curiosity world over. Two international conferences dedicated sessions on this very theme. In the meanwhile, we had also established that still larger (up to 40%) densification could be achieved on irradiation with energetic electrons and α-particles. And, the most satisfying supporting evidence was published by Venkatesan and Wilkinson of Bell Telephone Labs. who reported large (~40%) densification in a-Ge-Se films irradiated with energetic helium and neon ions. Figure 14 shows our data on contraction effects as induced by photons, electrons and ions. With the supporting results, doubts of some scientists evaporated. We were considerably encouraged by J C Phillips of Bell Telephone Labs. who published several papers to explain our observations. In his *Phys. Rev.* **B26**, 3510 (1982) paper, on molecular model of Ge_xSe_{1-x} films, his opening sentence 'perhaps the most remarkable photostructural transformation known in inorganic materials has been reported for obliquely deposited non crystalline Ge_xSe_{1-x} semiconducting film' by IIT Delhi group was a source of encouragement. According to Phillips, the films formed

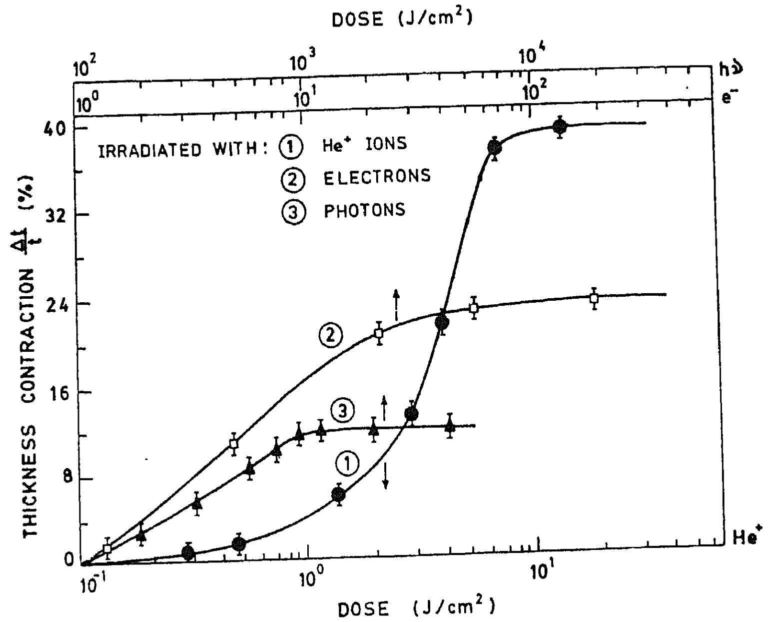

Figure 14. Photocontraction effect in 80° obliquely deposited ~ 1/μm thick a-Ge_{75}-Se_{25} films as a function of irradiation with energetic He^+ ions, electrons and band gap photons.

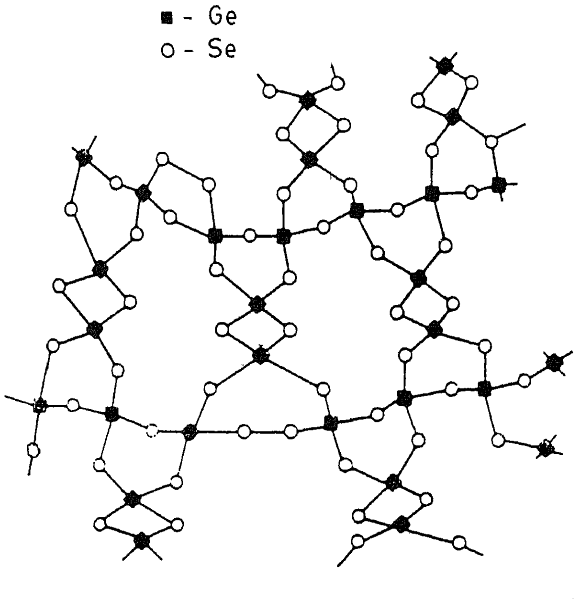

Figure 15. Molecular model of obliquely deposited amorphous Ge–Se films exhibiting giant photocontraction effect.

chain-like rafts (figure 15) which re-arranged drastically to minimize volume as the bonds broke on irradiation with energetic particles. The process is rather complex and its discussion cannot be pursued further in such a lecture. However, an important observation was made that the structure resembles a polymer chain and thus such films are the only known examples of an inorganic polymer.

5. Metallopolymer films

On returning from USA to join the Physics Department of IIT, Delhi on August 24, 1970, I was provided with an empty laboratory and a keen research student awaiting anxiously to be my first PhD student. Given such circumstances and my fanatic commitment (which brought me back to India) to experimental and applied physics, I posed the student the challenge of preparing epitaxial films of PVC by a novel chain-by-chain solution growth process. Excellent quality films were obtained by dipping suitable substrates in different strength solutions of PVC in various solvents. In fact, this became the first known example of epitaxially grown PVC films. The parabolic rate of growth of the films yielded on saturation a well-defined thickness. The technique was easily extended to a number of other polymers, e.g. PVA, PVB, PVAC, etc by both my student and a host of other investigators. It continues to be a commonly used technique even today.

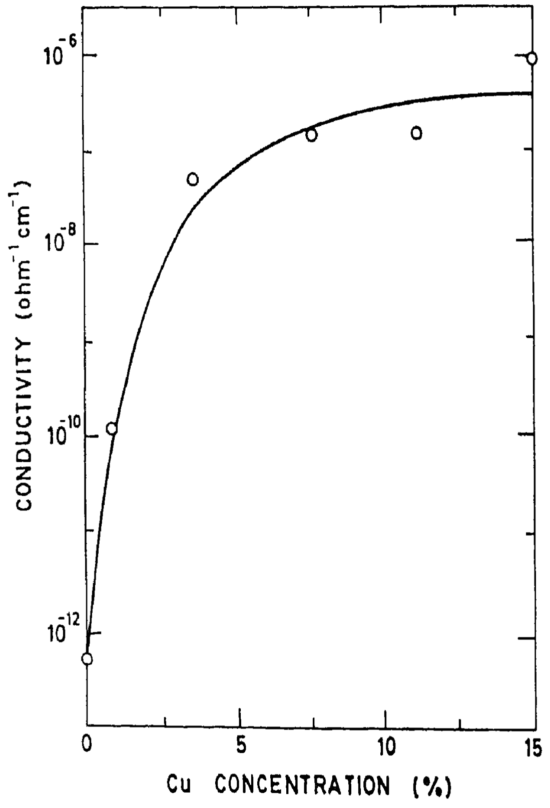

Figure 16. Variation of resistivity of solution grown PVC: Cu films as a function of copper concentration (in solution).

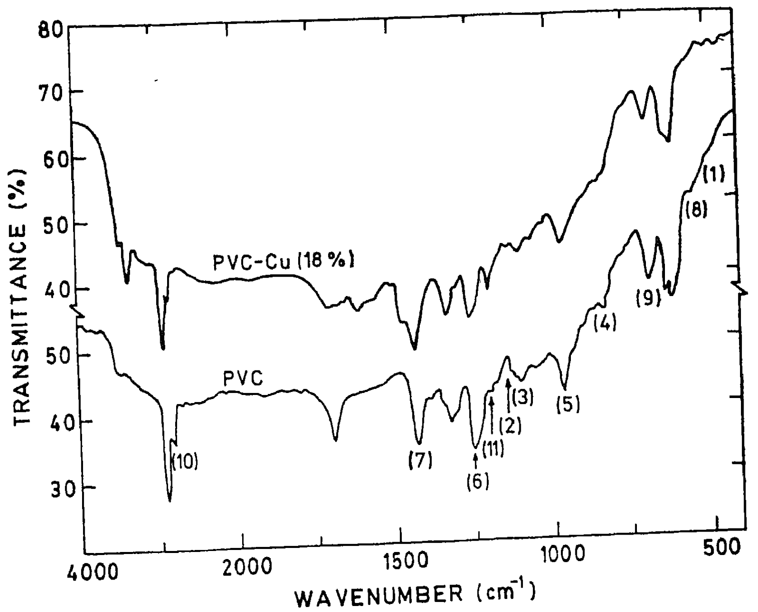

Figure 17. Infrared spectra of solution grown PVC: Cu films. The numbered absorption peaks have been identified due to various modes (See Rao and Chopra 1978).

Having deposited polymer films, we became interested in developing conducting transparent polymer films for our thin film solar cells. The solution growth technique using homogeneous mixture of polymer solution and a solution containing metal ions was effectively utilized to incorporate metal ions at the ends of the polymer chains as also to entrap between the chains. Thus, highly conducting metallopolymer films such as PVC doped with Cu, Ni, Fe etc were obtained. A typical resistivity variation of such a film with Cu concentration in the solution is shown in figure 16. The saturation of conductivity is due to the fact that it is not possible to introduce copper in PVC beyond a certain concentration. That copper is present at various sites (as per the interpretation of the spectra) in the PVC structure is clearly indicated by the complex IR spectra shown in figure 17.

6. Solution growth of semiconductor films

Applications of large area semiconductor films demanded simple chemical technique for deposition. In a chemical reaction in a solution, the anions and cations may combine to form a required alloy/compound depending on the relative values of solubility product vs ion product. Such a process has been known and used empirically for preparing PbS and CdS films. We undertook to explore the electrochemical aspects of the reaction. In this process, we established what may be called an electrochemical phase diagram (see figure 18). It is seen that by varying the relative pH values of the solutions, it is possible to obtain powdery, or coherent films with both normal and polymorphic structure of CdS. Similar diagrams can be established for a whole range of II–IV and II, VI and III–V compounds, and their alloys. This simple and inexpensive technique developed by us is being used extensively for obtaining

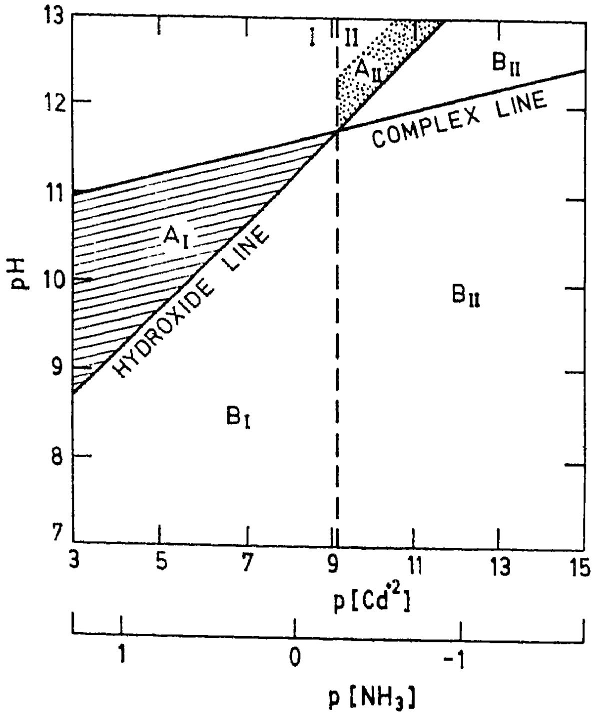

Figure 18. An electrochemical phase diagram for deposition of CdS films by solution growth process involving controlled reaction of $CdCl_2$ with thiourea complexed with ammonia. Hydroxide and complex lines for the reactants define various regimes for film and powder deposition.

CdS, ZnS and CdZnS films for thin film photovoltaic heterojunctions. We used the technique to deposit large area variable composition, multicomponent chalcogenide coatings for conducting electron and optical transport studies keeping in view a range of applications such as thin-film CdS/Cu_2S solar cells, photoconducting and photovoltaic infrared detectors based on Pb_xHgS_{1-x}, multilayered PbS/CdS interference coatings for optical selectivity required in photothermal conversion. By a suitable variation of deposition conditions, we were able to deposit α and β phases of Pb_xHgS_{1-x} films enabling a large variation of optical gap from 0·2 to 0·9 eV, as shown in figure 19. Besides polymorphic structures, the solution growth technique allowed deposition of metastable structures over a very wide composition range. And, thus, the technique offered a new frontier in materials science.

7. Optically selective coatings

One of the most important applications of thin films is in the area of providing spectral selectivity in the form of an appropriate reflectance/transmittance/absorption spectra. Whereas all materials—elemental, alloys or compounds—have intrinsic optical selectivity, it is desirable to tailor optical selectivity (for specific applications) by using tailored materials with specific optical constants. The process of deposition of thin films allows this to be achieved in several ways which were explored by us. By mixing two or more materials homogeneously or heterogeneously (on the scale of a fraction of the

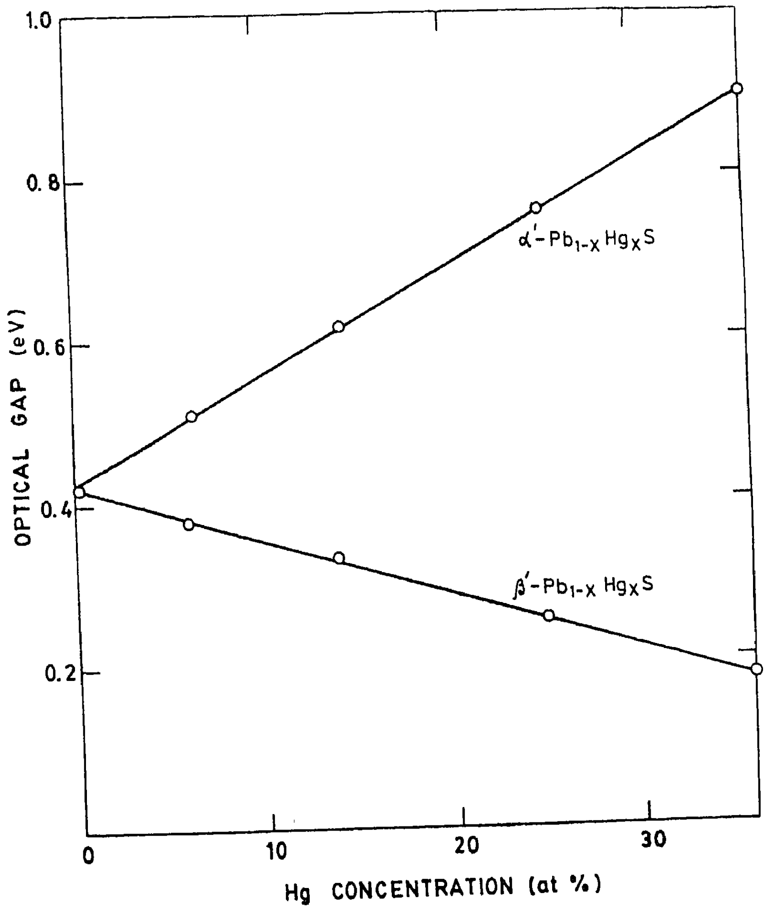

Figure 19. Variation of the optical gap of α and β polymorphous (cinnabar and zinc blende structures) of $Pb_xHg_{1-x}S$ films prepared under different pH conditions by solution growth process.

wavelength of the light used), one could vary optical constants as per effective medium theories. Figure 20 illustrates the variation of the refractive index of films of such a mixture of ZnS and Na_3AlF_6. Such experiments verified the applicability of simple Lorenz–Lorentz theory. By varying the composition spatially, we could obtain any profile of refractive index. In such a system, scattering from grains can be significant ($\sim 1\%$). One can obtain nearly zero scattering by using multilayers of two or more materials with appropriately varying thickness so designed that a particular spatial profile of the effective optical constant is obtained. We conceived and pioneered this technique around 1972. By using very simple manually controlled shutters, my research student (V N Yadav) was able to deposit (by vacuum evaporation) multilayer films with linear, parabolic or exponential index profiles with thirtyfive films. A typical example of one such unit (period) is shown in figure 21. This unit/period, a part of 10 such periods, was designed and fabricated to yield a high (99·9%) reflection interference mirror for lasers. Its characteristics are shown in the inset of figure 21.

Very appropriately, we called our optically selective composite film as 'multilayer coatings'. The present day name for such periodic layers is 'superlattice'. If a proper

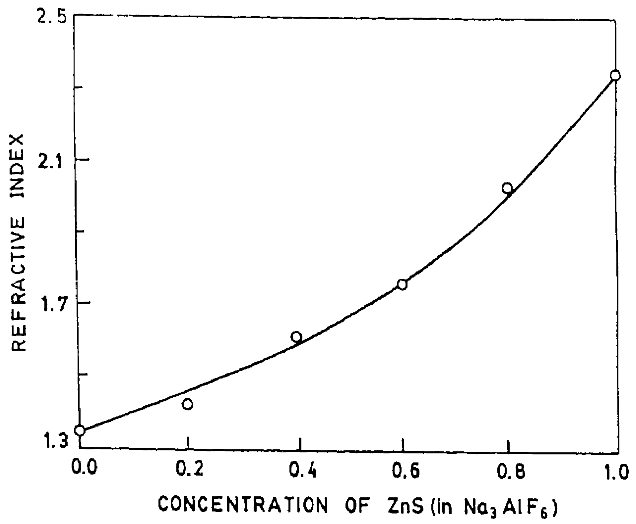

Figure 20. Variation of effective refractive index with ZnS concentration for atomically codeposited, ZnS and $NiAl_3F_6$ films obtained by thermal evaporation.

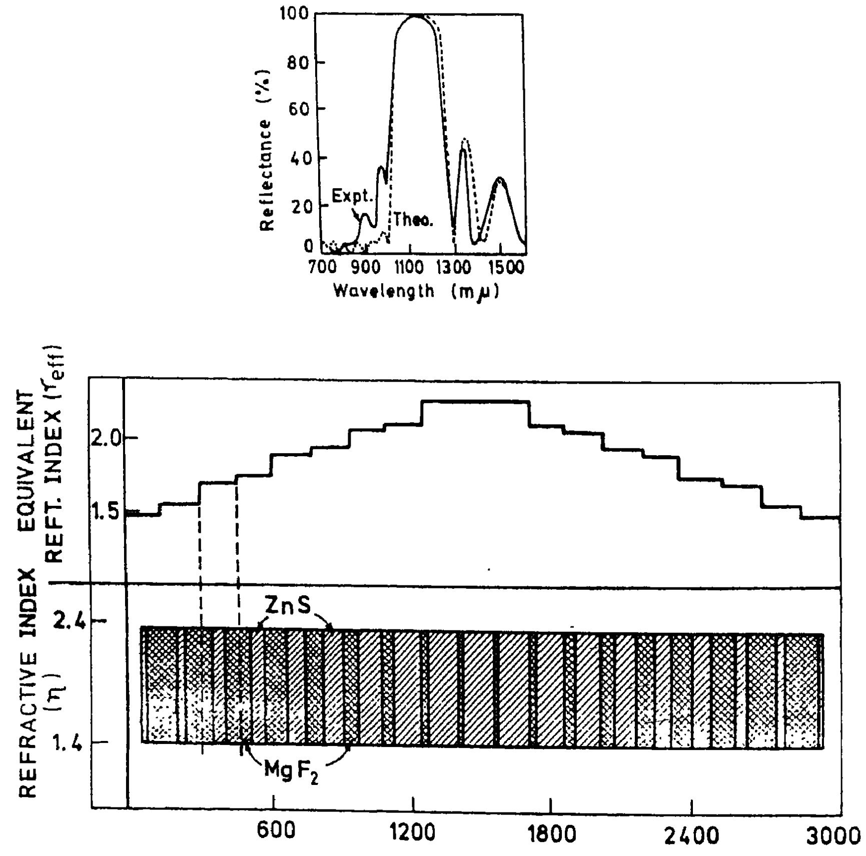

Figure 21. Effective refractive index profile (spatial) of a multilayer structure consisting of 35 alternate films of ZnS and MgF_2 of varying thickness calculated to yield a linear profile as shown. The reflectance spectrum of a 'superlattice' consisting of ten periods of such multilayers to yield an interference filter is shown in the inset. Theoretically calculated spectrum for such an interference filter is also shown by dotted lines.

history of science were to be written, we would be credited with being the first anywhere in the world to use the concept of 'superlattices' to tailor optical properties of coatings.

With increasing commercial interest in the photothermal conversion of solar energy, need arose for the development of simple and economical processes to prepare large

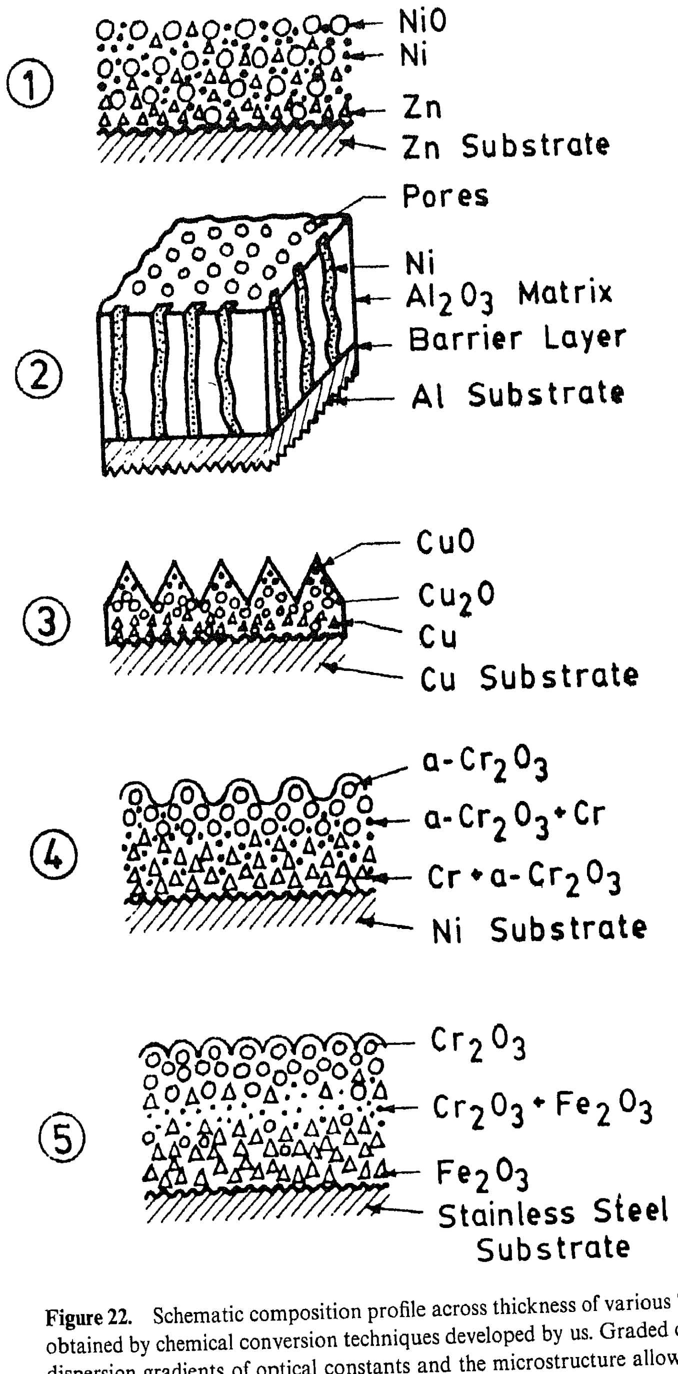

Figure 22. Schematic composition profile across thickness of various 'black' metal surfaces obtained by chemical conversion techniques developed by us. Graded compositions provide dispersion gradients of optical constants and the microstructure allows resonant scattering and photon trapping. All these surfaces have exhibited solar absorptance ranging from 95 to 99% with emittance ~0·1–0·3 at 100°C.

area surfaces with nearly total absorption of solar spectrum, along with insignificant thermal emittance (in the infrared region) at elevated temperatures. This led us to develop simple chemical conversion techniques to convert the surface of a variety of metals (e.g. Cu, Ni, Al, Mo, stainless steel, Co, Zn) to a graded mixture of metal and oxide of appropriate thickness and topography, as shown in figure 22. Such structured surfaces utilized interference, multiple scattering, and plasma resonance effects to yield desired selectivity of ~99% solar absorptance with ~0·1% thermal emittance at 100°C. In order to understand the optical behaviour of such coatings, comprehensive modelling of these coatings in terms of effective medium theories (e.g. Maxwell–Garnett, Bruggemann etc.) were carried out. As a result, commercially viable processes for 'black' metal surfaces were developed and 'black Cu' process was transferred to the industry. Large area solar collectors were fabricated and investigated for field applications.

8. Transparent conductors

Energy crisis world over provided a strong impetus to develop simple and cost-materials-energy effective large area thin-film devices for photothermal and photovoltaic conversion of the 'abundant' solar energy. Thin film solar cells (such as Cd/Cu_2S, a-Si:H, CdS/CdTe, $CuZnSe_2$/CdS) required transparent conductors—materials with dielectric-like properties—in the visible part of the solar spectrum and metallic behaviour in the very long wavelength regions. Films of oxides of indium and tin, with controlled deficiency of oxygen and with suitable dopants satisfy these conditions in principle. To translate the concepts to reproducible and stable large area coatings required the development of such techniques as spray pyrolysis and solution growth (very similar to that used by us for semiconductors), and a comprehensive understanding of optical absorption processes and electron transport processes in polycrystalline oxide films. Several research students worked in this exciting field and contributed to a large extent of what is known of transparent conducting oxides today in the published literature. The roles of oxygen vacancies and dopants on structure, microstructure, stability (temporal and thermal), impurity and grain boundary scattering of conduction electrons, grain boundary barrier heights, plasma resonance effects, and their dependence on dopants, degenerate semiconductor behaviour, energy band diagram, optical absorption processes and shift of the optical absorption edge due to shift of the Fermi surface as also the electron–electron coulombic interactions were established. These studies allowed optimization of electronic and optical properties and also the position of the plasma resonance edge (which determines the transparency cut-off wavelength).

An industrially significant outcome of our work was the development of spray pyrolyzed In and Al doped zinc oxide transparent conductor films with acceptably good electro–optical properties, and excellent stability of the film in a hydrogen bearing plasma (such as used for deposition of a-Si:H and a-Si_3N_4:H films). Our ESCA studies showed conclusively that the conventionally used tin and indium oxide films get reduced to metallic surface layers in the presence of hydrogen plasma. In contrast, spray pyrolyzed zinc oxide films were stabilized by the formation of OH bonds on the surface. These findings have led to the commercial utilization of these films in a layered structure with controlled roughness for a-Si:H solar cells. Figure 23 shows a typical spectral dependence of the transmission and reflectivity of antimony doped spray

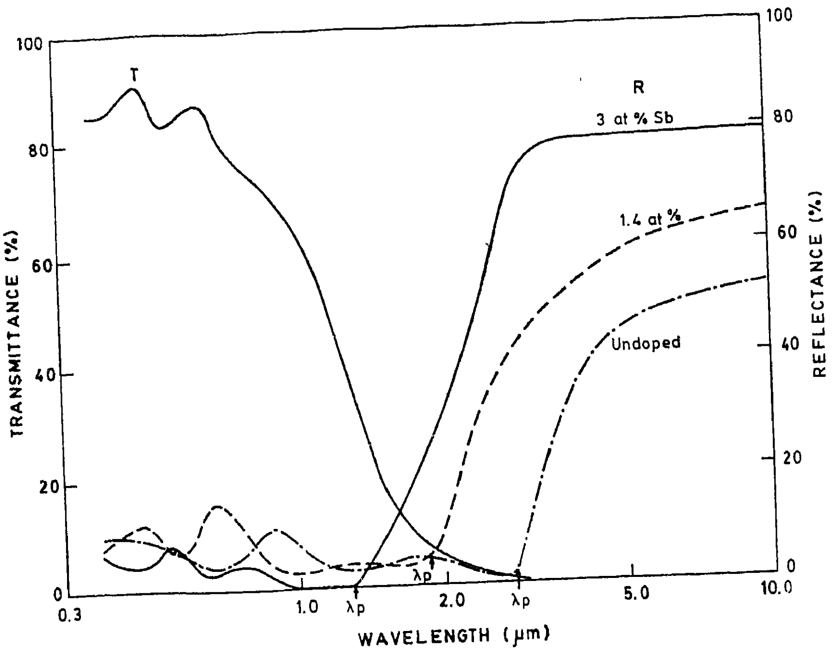

Figure 23. Spectral dependence (with interference effects) of the reflectance and transmittance of spray pyrolyzed SnO_x: Sb films for several Sb concentrations. The reflectance minimum is due to plasma resonance edge and is shifted with increasing concentration of Sb.

pyrolyzed tin oxide films. Similar results are exhibited by doped indium and zinc oxide films.

9. Thin film solar cells

Looking for a cost effective solution to photovoltaic conversion of solar-energy, the obvious answer is to exploit appropriate thin film junction solar cells such as CdS/Cu_2S, $CdS/CuInSe_2$, GaAs-based, a-Si:H based, CdS/CdTe, etc. This required development of viable large area deposition processes, suitable properties of the films and junctions. A successful process, called 'clevite process', of converting chemically the surface of CdS to Cu_2S to form a heterojunction providing ~5% photovoltaic conversion of solar energy was developed in the 60's. Our research group conducted extensive work on spray pyrolyzed and thermally evaporated CdS films, converted on the surface by a wet chemical, and a dry solid state reaction (with evaporated CuCl films) process. Although we succeeded in fabricating ~10% efficiency small area solar cells, it was not possible to arrest degradation of the efficiency which went down to ~6% over a short period, despite using a variety of new chemical and metallurgical concepts to minimize migration of Cu in grain boundaries of CdS. This part of our research has indeed been disappointing.

Spray pyrolysis was exploited to develop a new material namely $CuInS_2$ junctions with CdS yielding ~5% efficiency solar cells with vastly improved degradation characteristics. This material has attracted attention recently.

With the promising discovery of a-Si:H based thin film homojunctions for photovoltaic conversion our research group joined a nationally coordinated (along with groups at IACS, Calcutta and Pune University) programme on the subject. Our primary role was to develop glow discharge deposition technique, characterize *i*, *n* and *p*-type films and $p-i-n$ junctions thoroughly and to investigate photo-induced Staebler–Wronski (SW) degradation effect on a-Si:H based $p-i-n$ solar cells. We contributed significant information on the effect of deposition parameters on the photo-electronic and structural properties of the films and thus on the performance of solar cells fabricated with these films. It was thus possible to prepare ~ 8–10% efficiency cells. Unfortunately, the rapid photo-induced degradation of the performance of these cells continues to challenge us even today. By having a microstructure which is a mixture of amorphous and nanocrystalline plasma, we have shown considerable reduction of the SW degradation effect.

A noteworthy experiment was to use an ion beam to sputter silicon and to incorporate hydrogen and other dopants in the sputtering process without exposing the films to a plasma so that properties could be controlled more effectively. We succeeded in depositing good quality a-Si films and were able to incorporate hydrogen and nitrogen into the films by mixing these gases with argon—the glow discharge gas used for creating ions for sputtering. It was thus possible to obtain good quality a-Si:H:N films, with optical band gap going up to ~ 2·2 eV. The electronic properties of these films have not been found to be good enough for efficient solar cell applications.

10. Plasma processed hard coatings

Gaseous glow discharge plasma, excited by dc, rf, microwave, electron cyclotron resonance (ECR) or magnetron-type sources, provides the simplest laboratory/technical plasma of good density ($\sim 10^{12}-10^{5}/\mathrm{cm}^{3}$) to allow extraction of ions (of the glow discharge gases) to bombard and sputter a given target to deposit films atomistically onto a suitable substrate. Although known for almost a century, the technique received serious attention only in the early sixties. And we were there to play a key and pioneering role in developing such concepts as ion beam sputtering, sputter quenching, very high rate two chamber rf magnetron sputtering, and plasma assisted physico-chemical and sputter-chemical depositions. Four industrially significant US Patents based on this work have been obtained.

We have used plasma for over three decades to exploit its unique features of providing a medium for energetic, active and reactive, and charged (both positive and negative) atomic/molecular/radical species. Because of the interaction of these species with other gaseous or sputtered species introduced into the plasma, one observes a myriad electronic/chemical reactions such as excitation, ionization, dissociation, association, exchange, etc. As a result, a well-controlled plasma is a zoo of all possible, stable and metastable, species undergoing rapid dynamical changes under nonequilibrium conditions. It is these properties of the species which we have effectively used by clever experimental set-ups, to create a range of new, stable and metastable nanomaterials in thin film form. We have thus been able to create hard thin films of oxides, carbides, nitrides, borides and silicides of a number of transition metals which are well suited for tribological, wear and tear, protection and decoration applications of commercial interest. All these studies called for comprehensive investigations of structural (physical, topographical, chemical, metallurgical and electronic), optical, microhardness and tribological properties of the films and their interrelationships.

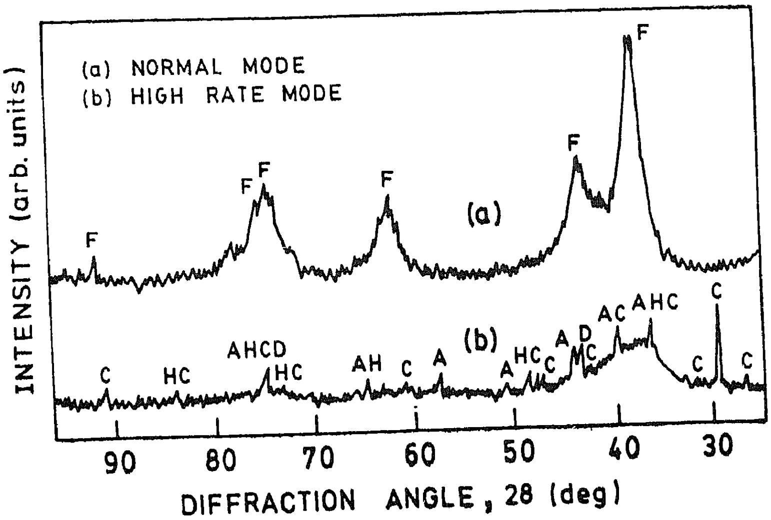

Figure 24. Grazing angle incidence X-ray diffractogram of reactively sputtered W–C films prepared under normal rf magnetron mode and a two-chamber high rate mode. The diffraction lines correspond to: (A) A – 15 W_3C; (C)–graphitic carbon; (D) diamond carbon; (F) FCC WC_x; (H)–hexagonal WC structure.

Grazing angle incidence X-ray diffraction, electron energy loss spectroscopy and spectroscopic ellipsometry techniques were among the new techniques exploited by us to analyze thin hard coatings.

The complexity and variety of structures so easily obtained in a plasma process is illustrated (figure 24) by the grazing angle incidence X-ray diffraction pattern of W–C films obtained by magnetron sputtering of tungsten and allowing the sputtered species to react with species within a hydrocarbon-based plasma (using for example CH_4). By changing the angle of incidence of X-rays, one observes that there exists a composition gradient across the thickness of the film. By choosing appropriate deposition parameters, it is possible to produce nearly single phase WC films of good hardness.

That one can vary the composition of the films, over a large range is illustrated in figure 25 for the case of deposition of Cr–C and Cr–N films, by sputtering Cr in the presence of acetylene and ammonia plasmas. Among the various parameters, the composition can be varied most conveniently by changing the deposition temperature. Both carbon and nitrogen are incorporated into chromium, first interstitially (forming a saturated solution) and later as different compounds. As expected, the hardness (figure 26) depends on the structure and shows a maximum for a saturated solution. Similar results were obtained for carbides and nitrides of titanium.

Because of its very high hardness, the cubic polymorphic form of boron nitride coatings is of special interest. By evaporating boric acid H_3BO_4 (a cheap and commonly available material) which breaks up into B_2O_3 and then subjecting the vapours to ammonia plasma, along with electron bombardment, we developed a method to prepare nearly pure cubic boron nitride films of VHN ~ 2000. This process is of considerable commercial significance and has been patented.

Hard coatings (based on W, Mo, Ti and Cr) developed by us have been applied to machine tools and their tribological and wear–tear properties have been examined.

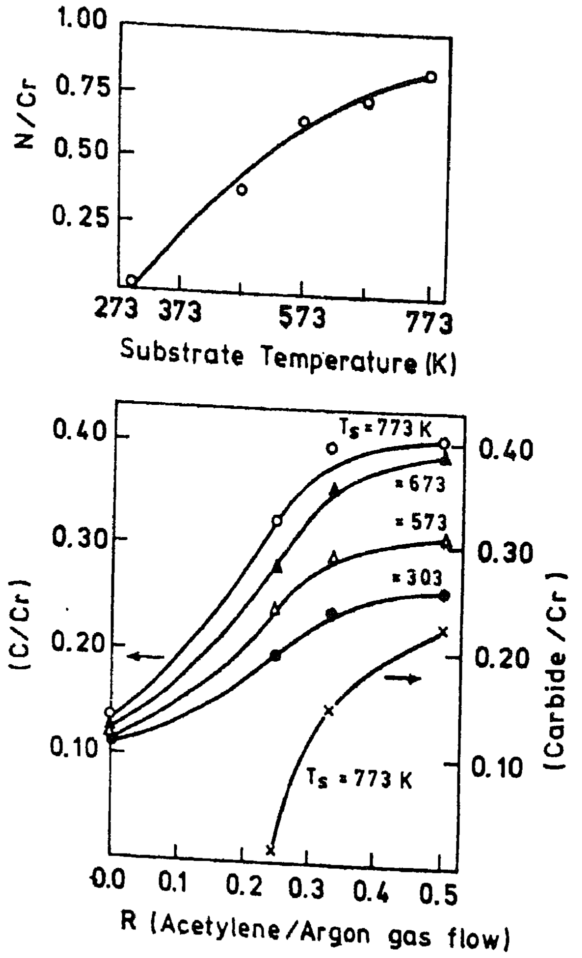

Figure 25. Variation of nitrogen and carbon in reactively sputtered chromium films as a function of substrate temperature and concentration of acetylene in argon gas for sputtering. Also shown in the concentration of carbide in the Cr–C films deposited at 773 K.

'Whether mechanical hardness has anything to do with the optical properties of a material has been examined by us. In principle, there should be some correlation through the electronic properties. Our studies have established for the first time that at least for some cases of carbides and nitrides of Wand Cr, and oxides of tin and indium, there is an apparent correlation between the dielectric function, plasma resonance edge and the microhardness. Admittedly, this is a speculative hypothesis but it is one which I hope will receive further attention by other workers.

To complete the story, I should also say a few words about our extensive work on silicides which is of direct interest to the technology of contacts and interfaces in fabrication of silicon devices. By sputtering single and multilayers of Pt, W, Mo and Ni on silicon at different temperatures the formation and growth of various silicide compounds has been studied. Our studies have shown that only under very specific conditions, a particularly useful single phase silicide can be obtained. Also, using two layer metal films, stable and good quality silicides are possible.

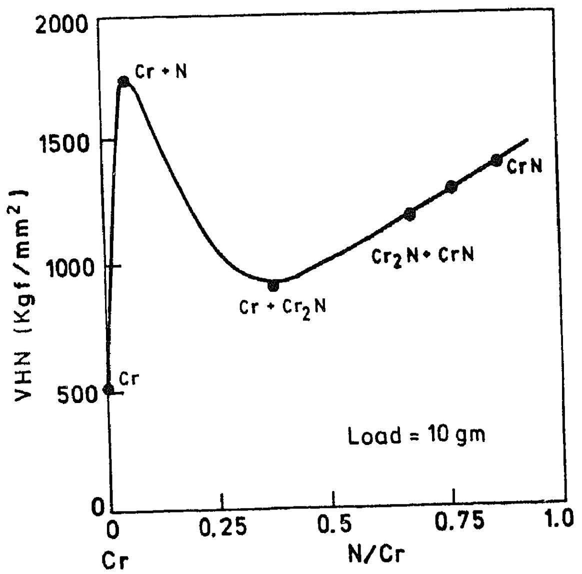

Figure 26. Variation of Vickers microhardness (VHN) of thick ($\sim 1\,\mu$m) reactively sputtered Cr–N films as a function of N/Cr ratio.

11. High T_c superconducting films

The discovery of high T_c oxide superconductors brought our research group into the nationally coordinated project with a focus on development of thin and thick films of the high T_c materials so that appropriate electronic applications could be demonstrated. We have developed novel coprecipitation and pyrophoric synthesis techniques to prepare yttrium- and bismuth-based nanomaterials which have been used to prepare wires, tapes, thick films as also targets for sputtering. We have contributed towards new compositions for high T_c superconductors, understanding of the effect of additives, fluctuation phenomena near transition temperature through thermopower studies, sintering and crystallization effects and techniques for producing tapes with critical current density exceeding 10^3 A/cm^2 at 77 K.

Our thin film work has concentrated on Y–Ba–Cu–O system. RF sputtering and molecular beam epitaxy (MBE) techniques have been used to grow polycrystalline and epitaxial films on a variety of substrates (e.g. YSZ, MgO, silicon, $SrTiO_3$) with and without interfacial layers (for improving the structural quality and superconducting characteristics of films and for preventing substrate diffusion). Plasma diagnostic techniques were employed to understand the large sensitivity of the properties of films to deposition conditions. A correlation between the superconducting properties (T_c and J_c) and plasma ion density was established. The beneficial effects of high pressure and off axis sputtering were provided scientific basis by the diagnostic studies. Further, the spiral growth of films with catastrophic roughness effects on films was modified by providing more nucleation centres and thus films with rms roughness of 100 Å (see figure 9) were obtained. Besides a good and sharp T_c, a high ($\sim 10^6$ A/cm^2) J_c thin film for Josephson junction devices must be stable and smooth to within the coherence length ($\sim$ 10A). Despite our progress in achieving rms roughness which are among the lowest reported in literature, we have some way to go to achieve atomic smoothness.

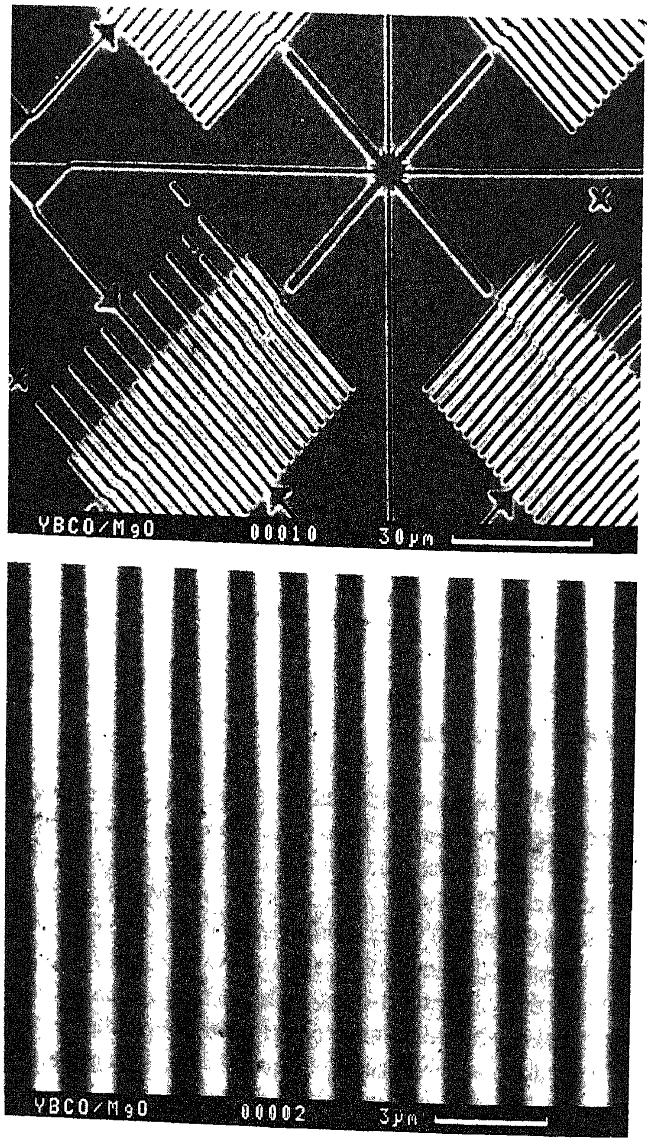

Figure 27. Microlithographically patterned micron size YB Co films for device applications.

Nevertheless, our studies have indicated what experimental approaches have to be taken.

Microlithographic technique using EDTA etchant has been developed to fabricate ~ 1 μm line patterns as shown in figure 27. Simple rf SQUID structures have been fabricated and their performance has been demonstrated. Also, patterned films have been used for detection of microwaves.

12. Epilogue

I have given a bird's eye view of the major achievements of our researches during the last thirtyfive years. Covering a very large and wide canvas, my students, colleagues and

I have established many new milestones in thin-film deposition techniques and processes, physics of the nano-state and a whole range of applications in many diverse optical, electronic and mechanical fields. That we could start from a zero level to create world class facilities, conduct pioneering R/D work to push the frontier of the science and technology of micro/nano-materials at both academic and industrial levels, should hopefully provide an inspiring example of a focussed collaborative and cooperative work. I dedicate this lecture to the spirit of cooperation—so essential for effective high-tech experimental work today.

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