I

INTRODUCTION

CHAPTER-I

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1.1 INTRODUCTION

The research on the physical properties of the matter has progressed so much during the last hundred years that today physics is divided into a large group of special branches which are often very distant from each other. These branches arise because of the vast extent of the science itself and are distinguished by the particular areas studied, the method of research and so on. An independent and important branch that has developed recently is the physics of the thin films (T.F). This deals with the systems which have only one common property namely, that one of their dimensions is very small, though all other physical properties may differ as well as method of research.

Rapid development of thin film technology makes application of thin films appropriate in microelectronics, integrated circuits and in field of superconductivity and superconducting devices. In all these applications of thin films, substrates for thin films plays a very important role. The characteristics of the films, good quality with reproducible results depend on the properties of the substrates. In all, substrate plays a role of "man behind the curtain". Substrate accompanies the thin film from "cradle to grave" even though it is only obliquely referred.

1.2 REQUISITE PROPERTIES OF THE SUBSTRATES

We can define substrate as the mechanical supporter for thin films. In electronic applications the substrate serves as an insulator. For modern thin film (T.F) technology applications substrates are required to fulfill some requisite properties as given below.

1) For long term stable thin film properties, it requires that no chemical reaction takes place with the substrate materials.

2) Thin film technology demands that with good mechanical support, substrates should provide an adequate adhesion to the thin films.

3) The substrates should be chemically inactive with thin film material and provide a good mechanical support with an adequate adhesion to the thin film not only at normal temperatures, but also during

relatively large temperature changes. These temperature changes may arise during the preparative stages such as,

- i) Annealing at higher temperature,
- ii) Degassing at higher temperatures and
- iii) During deposition on heated or cooled substrates.

4) During the operation of electronic elements to keep the constant temperature of the surface, a sufficient heat removal is necessary which demands that substrate material to have proper heat conductivity.

5) To produce thin films with defined and reproducible electrical and other parameters, substrate surface should be flat and smooth i.e. mirror polished.

6) For a defined growth of monocrystalline-epitaxial films certain crystal structure and orientation of the surface plane of the substrate surface is usually needed. Which demands surface of the substrate to be with abscence of contaminations.

1.3 SUBSTRATE MATERIALS

In general there is no such material that would satisfy all the requisite properties. For single-crystal epitaxial growth, the most frequently used materials are the single crystals of alkali halides, silicon, germanium, sapphire and mica etc. With all these, the most widely used substrates for polycrystalline films are glasses, ceramics, organic materials and metallic foils.

Glasses : For glass substrates alkali contenst are very important especially sodium is used in pyrex or fused silica. i.e. 80.5% SiO_2, 12.9% B_2O_3, 3.8 % N_2O, 2.2% Al_2O_3 and 0.4% K_2O. The glass substrates which are i) chemically in active ii) temperature resistive to a considerable degree causes the instability in the electrical and other properties of the films with higher conentrations of Na_2O. Na_2O is practically immobile upto 4%. Above 4% of Na_2O at higher temperature and electric fields it can easily move in the glass. This together with moisture it forms a layer of high conductivity on the surface and causes electrolytic corrosion of the film.

Ceramics : Ceramics are the substrates prepared by sintering methods. Even though with same content of alkali metals, they can stand with high temperatures. These have advantages over the glass ones due to their i) Higher mechanical support ii) Thermal resistance and iii) Thermal conductivity. But these have a lower quality in smoothness of the surface, which is affected by the sintered grain structure. But a considerable .... smoothness can be achieved by producing fine grained ceramics.

Organic Materials : Organic materials have advantages of having low specific weight but cannot stand for higher temperatures. So they are used in special cases. Example (Mylar or Teflon).

Metallic Substrates : Metallic substrates are usually used in electro deposition as conducting cathode for deposition of metallic films. Among the different classes of possible substrates the metal substrates which are due to their malleable and ductile characteristics, form an interesting class. In HTc super conductors they offer hope for development of replacements for tape and wire, which have been difficult to realise in due to their brittle ceramic charater.

Substrate materials particularly used in High Tc super conductors are MgO, $SrTiO_3$, YSZ etc in single crystal form and in pellets (sintered) form.

1.4 ROLE OF THE SUBSTRATES ON THE PROPERTIES OF THE FILMS

Highly cleaned and polished smooth surfaces of single crystals or polycrystalline nature are required for the growth of thin films of particular orientation. Surface impurities of the substrates influence the binding energy between the deposited substance and the substrate, and so the size and growth conditions of critical nuclei. Impurities built directly into the film may influence its resistivity and magnetic properties.

Further, impurities on the substrates may considerably alter the adhesion of the film to the substrate. The adhesion will be strongest when a layer of compound, e.g. oxide forms in between the film and substrates. Example in the case of iron or aluminium on glass. Adhesion will be much weaker if the binding consists of only Van-Der-Waals forces.

Even though the compound layer is not formed between the film and substrate, good adhesion may be achieved by a transition layer grown by mutual diffusion. This has been demonstrated for example on Cd-Fe a combination which normally shows weak adhesion. If however, the film is prepared by cathode sputtering the impinging particles have a higher energy so that the surface is cleared of oxides precluding mutual diffusion. The deposition centers have higher binding energy, and finally, the particles themselves penetrate the surface to a greater depth. All these factors in cathode sputtering result in enhanced adhesion of the film with substrate.

Properties of the films were found to be highly sensitive to the choice of the substrate material. For example Narottam P. et al (36) have reported that the film of (YBCO) on Ba-Ti turned green after firring due to a reaction with substrate material. A film on Ni-Al-Ti has a Tc (onset) 95K and lost 90% of its resistivity at 75K. However, even at 4K it was not fully superconducting. Possibly due to a reaction between the film and the substrates and inter diffusion of the reaction product. The film on the alumina had Tc(onset)~96K Tc(zero)~ 66K & ΔTc(10-90%)~10K. Best film was obtained on spinel and had Tc(onset)~94K and zero resistance Tc(zero) at 81K and a transition width (10~ 90%) of 7 K. The films has excellent adhesion with all the susbtrates.

For application such as in microwave of HTc superconductors even though YBa_2CuO_{7-x} (YBCO) can be developed successfully on $SrTiO_3$, MgO and YSZ with Tc° arround 70K. These are found unstable for microwave applications. It has been reported that $SrTiO_3$ has sharp dc resistance transitions whose lattice dimensions match closely with YBaCuO. However, $SrTiO_3$ has high dielectric loses and excessively high dielectric constant (ϵ = 3000 at 77K). Eliminates this substrate as a candidate for microwave applications. Ref(32). Ysz also exhibits high dielectric loss. MgO having reasonable electric properties, is chemically unstable and easily cleaves.

In ref(32) R. Brown et al have reported that strontium lanthanum aluminate ($SrLaAlO_4$) has considerable potential as a substrate material for high temperature superconductor (high Tc microwave applications). Excellent lattice match is obtainable on a 0.4° tilt from the c-axis. The lattice dimensions encourage ab plane epitaxial growth. The thermal expansion was found to be 7.4 x 10^{-6} $^{\circ}C^{-1}$. The combination of relatively high dielectric constant and low loss makes $LaSrAl_2O_4$ a very attractive candidate for selective microwave application.

Superconducting (35) Y-Ba-Cu-O thick films with preferred c-axis orientation were obtained by screen printing method. Thick films with preferred c-axis orientation appeared only when the substrate material was YSZ, the film thickness was around 10μm and the film was fired at 980°C for 6mins. The preferred c-axis orientation was caused by an interface reaction between the Y-Ba-Cu-O thick film and the YSZ substrate. The superconducting characteristics of the thick films were Tc zero = 98K and Jc (77K) = 7 A/cm^2.

1.4.1 SUBSTRATE TEMPERATURE

Substrate temperature plays an important role in thin film technology. Depending upon the method of deposition, range of temperatures for substrates is changed.

In vacuum evaporation deposition, melting point of the substrates should be higher than those of the evaporant materials to be deposited. At the deposition temperature substrates should be chemically inactive with the evaporant material.

Depending upon the substrate temperature, crystallinity of the deposited thin film will be changed. In general it is classified that at lower temperatures of the substrates deposition will be amorphos but some metals even at room temperature they form polycrystalline structure due to their closed packing. At intermediate temperature of substrate, thin film form the polycrystalline structure and at higher temperatures of substrates they form the single crystalline structure.

These temperatures are measured with respect to melting temperature of the evaporant material (Tm). 1/3 and 2/3 values of Tm discussed by Komnik(52); 1/3 Tm limit is essentially that below which the adatoms donot have sufficient mobility to produce ordered structure and the condensation mechanism may be denoted as vapour-disorded solid. For ordered structured it is required that the deposits are annealed at higher temperatures. 2/3 Tm is however, a significant parameter since it is nearly the melting point of ultrathin films of various metals.

Bruck(53) examined the effect of temperature of the substrate on the epitaxy growth of fcc metals and concluded the existance of a critical temperature and called it as "epitail temperature" above which epitaxy is perfect and below which it is imperfect. Even though an epitaxial temperature does exists for a system, it is not just a characteristic of the deposit-substrate system but also strongly depends on the deposition conditions.

An increasing substrate temperature may improve epitaxy by

i) Aiding the desorption of adsorbed surface contaminants.

ii) Lowering supersaturation, thus allowing the dilute gas of adatoms sufficient time to reach the equillibrium positions.

iii) Providing activation energy for adatoms to occupy the positions of potential minima.

iv) Enhancing recrystallization due to the coalescence of islands by increasing surface and volume diffusion and,

v) Assisting a possible ionization of surface atoms.

These factors also depend on other factors of deposition condition making it difficult to define a precise value of the epitaxial temperature.

1.4.2 STRUCTURE OF THE SUBSTRATES

The structure of a substrate is an important property of a substrate since it is here that the film-substrate interaction occurs. Various types of irregularities make up the overall surface texture. The surface defects which will encounter are, point defects, dislocation lines and monoatomic edges on cleavage planes on atomic scale.

Polishing scratches, grinding scratches, crystalline boundaries in polycrystalline and pores on glass drawing lines are on sub micron scale. With these defects there will be defects on macro level. These defects depend upon the technique used to synthesis the substrate.

Polished single-crystal wafers have very uniform surfaces and yeild smooth traces. Drawn glasses and glazes have surface irregularities. These may be as high as 1000 A° and stem from the forming operations.

Sintered ceramic materials particularly alumina are of great practical interest because of their mechanical strength and high thermal conductivity. Polishing such materials does not significantly improve the surface because there is little cohesion between the grain boundaries. Hence, chipping occurs during the finishing operations. To overcome these limitations very fine grained ceramics are prepared. In addition to less textured surfaces, such bodies have higher mechanical strength and volume resistivity than large grained materials of comparable compositions.

In the preparation of thin film components for microelectronic applications, surface roughness and flatness are crucial properties. Flatness is required to facilitate close contact with photo masks and can be obtained satisfactorly with most substrate materials. The surface micro finish requirements however, vary with the film thickness to be deposited and are difficult to meet in cases where extremely thin films such as 100A or less are desired.

Even the best single-crystalline substrates acquire defects in the fabrication and manufacturing processes. These defects are propagated to the deposits as dislocations continue into epitaxial film.

Defects on the submicron scale such as fine scraches on silicon wafer surfaces also generate irregularities in thin films. Balk et al (55) reported that mechanical damage of the original surface affects the rate of oxidation.

In microelectronic applications, thin film resistors are relatively insensitive to surface roughness as long as the surface roughness does not exceed the film thickness. The rougher surfaces yield films of higher sheet resistances lower temperature coefficients and poorer stability during thermal aging.

For the film cpacitors, the dielectric films used are particularly sensitive to isolated defects. Since nonuniform electric field of such points are likely to cause dielectric breakdown. The properties of magnetic films are also affected by the treatment of the substrate, scraches in the substrate surface which will reduce the switchning energy. Local stresses affect the direction of magnetization so that the area surrounding the scratch resembles a Neel wall. The only difference being that the magnetization direction is parallel instead of antiparallel. Other magnetic properties such as magnetostriction and ferromagnetic resonances are also affected by surface roughness.

With surface roughness, porosity of the films also affects the substrate surface where pores intersect the surface, they retain dirt or contamination from cleaning solution. During subsequent vacuum processing, the release of occluded gases or decomposition of organic residues are often found to create problems in the thin film properties.

1.5 SUBSTRATES FOR SUPERCONDUCTING FILMS

Since the discovery of a new oxide superconductors by Bednorz and Muller (3) there have been a rush of new compounds with the higher critical temperature than triggering materials. Presently there exists five prominent high Tc systems namely the four cuprates formed with La(Tc = 30K to 40K), Y(Tc = about 90K), Bi(Tc = 80K to 110K) and Tl(Tc = 100K to 125K) and a non copper based system with Tc about 30K.

From the survey of these superconductors tabulated in Tables I and II it is clear that the Tc critical temperature of all these materials depend upon the substrate used. Since these discoveries, number of efforts have been made to prepare superconducting films with good qualities, such as high Tc, sharp transition, and high critical current density. It is well known that, reaction between deposited film and substrate at processing temperature degrade the superconducting properties. In order to obtain good superconducting films, it is necessary to understand and control the reaction between deposited film and substrate. Such type of reactions can be controlled by selecting proper substrate materials or by depositing layer of stable material between film and substance. Upto now number of research works have been reported of superconducting films on single crystal substrates like MgO, $SrTiO_3$, YSZ (Yattria stabilized zirconia) etc (6), (7), (8).

However, for industrial and electronic applications some inexpensive and easily available substrates are required. Recently, some research investigators, have prepared thin film of superconductor on to polycrastalline MgO and YSZ substrates. There are some reports on superconducting films on metallic substrates with barrier layers of Y-ZrO_2, SiO_2 and MgO barrier electrodeposited.

BiSrCaCu System

Sr. No.	Method	Substrates and Results Obtained	Form of the substrate
1	Screen Printing	MgO(100), Ag tape(107K) YSZ(68K), $SrTiO_3$(72K)	Single Crystals (38)
2	Laser Sputtering	MgO(100)(80K) ZrO (100)(80K) $SrTiO_3$(100)(10-20K)	Single Crystals (39)
3	Multilayer Deposition	α-Al_2O_3(0001) MgO(100)(80-70K)	Single Crystals (45)
4	Sol-Gel Method	MgO(100)(117K→84K)	Single Crystals (41)
5	rf Magnetron Sputtering	MgO(100)(100K)	Single Crystals (34)
6	Metallo-organic Complexes	MgO(100)(92K) Au, Ag ribbon (79K,85K)	Single Crystals and Polycrystalline ribbons (10)
7	Pulsed Excimer Laser Evaporation	$SrTiO_3$(100) 92K (Tc) Si, (YSZ) MgO(92k)	Single Crystals (6)
8	Magnetron Sputtering	MgO,(110) sapphire $SrTiO_3$	Single Crystals (44)
9	Electron Beam Deposition	$SrTiO_3$(100)92K	Single Crystals (43)
10	Chemical Vapor Deposition	MgO(78K)	Single Crystals (45)

Contd.....

Sr. No.	Method	Substrates and Results Obtained	Form of the substrate
11	Thermal Decomposition of metallic complex salts	MgO(77K)	Single Crystals (47)
12	Electro Deposition	FTO coated MgO(76K)	Pellets
13	Spin Coating	MgO(90K), $SrTiO_3$, Si, ZrO_2 as barrier layers 95K, 75K	Single Crystals Polycrystalline nature (33)

RaBaCuO System

Sr. No.	Method	Substrates and Results Obtained	Form of the substrate
1	Laser Deposition	$SrTiO_3$(100)-(90K→77K)	Single Crystals (25)
2	Pulsed Excimer Laser Evaporation	Si, YSZ, MgO(85K Onset)	Single Crystals (6)
3	Electron beam Deposition with single source	MgO, $SrTiO_3$ YSZ (86K)	Single Crystals (43)
4	Screen Printed	YSZ(78K) MgO, $SrTiO_3$(86K)	Single Crystals (48)
5	DC Magnetron Sputtering	MgO(78K)	Single Crystals (46)
6	EcR Ion Beam oxidation	SrTiO3(110)(100K) SrTi(100)82K	Single Crystals (49)
7	Electrodeposition	MgO Pellets 68K	Pellets Ceramic (50)
8	Laser ablation Sputtering	$SrTiO_3$(100) transition characteristic were observed at 4.2K with current and voltage gain exceeding one	Single Crystals (25)
9	Water Deposition	$SrTiO_3$(001) Josephson device operating at 80K YBaCuO-PrBaCuO-YBaCuO	Single Crystals (26)

Contd.....

Sr. No.	Method	Substrates and Results Obtained	Form of the substrate
10	Pulse layer Deposition	$SrTiO_3$ (001) substrate Multilayer YBaCu flux transformer	Single Crystals Polycrystalline with HTc SQUIDS. (27)
11	Laser process	$Y-ZrO_2$, Ag as barrier layer. A prototype HTc SQUIDS magnetron working at 77K	Polycrystallne (28)
12	Ion beam sputtering	Si substrates with ITO coated buffer layers	Single Crystal (37)
13	Screen printing	YSZ, MgO sapphire	Single Crystals (35)
14	Screen printing	Al_2O_3, MgO (Ni-Al-Ti) BaTi spinal YSZ(89K)	Single Crystals polycrystalline spinal (36)

1.6 STATEMENT OF THE PROBLEM

In the present investigation our goal way is to synthesis Sr-TiO_3 substrates for superconducting high Tc thin films. The alloyed films of Sr-Ti films have been planed to synthesised using electrodeposition technique.

Thin film structures prepared by electrodeposition have advantage of consuming the least raw materials and simple fabrication. In electrodeposition technique it is not necessary to start with very pure materials. It is an isothermal process mainly controlled by electrical parameters such as electrode voltage and current density. With optimising the molarity of the constituent electrolytes the above parameters can be easily adjusted to control film thickness morphology and composition.

Sr-Ti alloyed films have been planned to synthesis from aqueous and non-aqueous bases on to metallic substrates, such as stainless steel, copper, brass and flourine doped tin oxide coated glass substrates via electrodeposition technique. Alloyed films have been oxidised at higher temperatures inorder to obtain the oxide films. The films have been planned to be characterised by various techniques such as X-ray diffraction microstructural photography and electrical properties. The above properties have been studied in detail and reported.

REFERENCES

1) Shand, E.B., McGraw Hill Book Company, New York, (1958).

2) Handbook of thin film technology, Maissel and Glang, McGraw Hill Book Company, New York, (1970).

3) J.G. Bednorz and K.A. Muller, Z. Phys 13.64 189 (1986).

4) M.K. Wu, J.R. Ashburn, C.J. Torang, P.H. Hor. Phys. Rev. LeH, 58, 908 (1989).

5) H. Haeda, Y. Tanaka. Jap S.J. Appl. Phys. 27, 209, (1988).

6) E. Fogarassy, et al; Solid state comm, Vol.67, No.10 pg75 (1988).

7) K. Shinohara, F. Manukta and M. Yamanaka; Japs J. Appl. Phys 27 1683 (1988).

8) T. Akne and N. Sakamoto; Japs J. Appl. Phys. 27, 2084 (1988).

9) K. Nonaka, S. Hayasti et al; J. Mater. Res; Vol. 6, No.8, Aug (1991), p. (1750).

10) H. Gruber et al; Superconduting Bi-Sr-Ca-Cu-O. thin film; Phys. stat. sol(a). 126, 229 (1991).

11) M. Makheld, H. Eckhardi, Z. Iqbal; Appl. Phys. Lett, 54(19), 8, May, 1989, p. (1932).

12) S.B. Ogale, V.N. Konikar; Appl. Phys. Lett. 59(15), 7, October (1991), p. 1908.

13) B.M. Moon et al; P 1905 Appl. Phys. Lett. 59(15), 7, October (1991).

14) A. Oishi et al; P 1902 Appl. Phys. Lett. 59(15), 7, October 1991.

15) P. Liand et al; P 1064 Appl. Phys. Lett. 59(9), 26, August 1991.

16) M. de. keijser et al; P 3556 Appl. Phys. Lett. 59(27), 30, Dec 1991.

17) M.N. Kamalasanan, et al; P 3547 Appl. Phys. Lett. 59(27), 30, Dec 1991.

18) R. Ramesh et al; P 3542 Appl. Phys. Lett. 59(27), 30, Dec 1991.

19) F. Maeda et al; P 363 Appl. Phys. Lett. 59(3), 15 July 1991.

20) P. Tiwari, S. Sharan et al; P 357 Appl. Phys. Lett. 59(3), 15 July 1991.

21) M.L. Chu et al; P 1123 Appl. Phys. Lett. 59(9), 26 Aug 1991.

22) Hirolaka Tamura et al; P 298 Appl. Phys. Lett. 59(3) 15 July 1991.

23) C.H. Chen et al; P 2339 Appl. Phys. Lett. 53(23), 5 Dec 1988.

24) G. Koren, E. Polturak, B. Fisher et al; P 2330 Appl. Phys. Lett. 53(23) 5 Dec 1988.

25) K. Nonaka et al; P 1750 J. Water Res Vol.6 No.8 Aug 1991.

26) Akira Yoshida et al; P 1242 Appl. Phys. Lett. 59(10), 2 September 1991.

27) J.B. Barner et al; P 742 Appl. Phys. Lett. 59(6) 5 Aug 1991.

28) B.Oh. R.H. Koch et al; P 123 Appl. Phys. Lett 59(1), 1 July 1991.

29) Aiguo Feng et al; P 1248 Appl. Phys. Lett. 59(10) 2 Sept 1991.

30) K.P. Daly et al; P 543 Appl. Phys. Lett. 58(5), 4 Feb 1991.

31) B.J. Kellett et al; P 1143 Appl. Phys. Lett. 57(11), 10 Sept 1990.

32) R. Brown et al; P 1351 Appl. Phys. Lett. 57(13), 24 Sept 1990.

33) L.S. Hung et al; P 2450 Appl. Phys. Lett. 53(24), 12 Dec 1988.

34) K. Setsune et al; P 600 Appl. Phys, Lett. 53(7), 15 Aug 1988.

35) Junji Tabuchi et al; P 606 Appl. Phys. Lett. 53(7), 15 Aug 1988.

36) Narottam. P. Bansal et al; P 603 Appl. Phys. Lett. 53(7), 15 Aug 1988.

37) B.J. Kellett et al; P 1146 Appl. Phys. Lett. 53(11), 10 Sept 1990.

38) Kazutomo Hoshino et al; Japs J. of Appl. Phys. Vol.27 No.7 July 1988 PP L 1297 - L 1299.

39) Masaki Konata et al; Japs J. Appl. Phys. Vol.27 No.7 July 1988 PP L 1293 - L 1296.

40) Masataka Ohkubo et al; Japs J. Appl. Phys. Vol.27 No.7, July 1988 PP 1271.

41) Toshio Ko Bayashi et al; Japs J. Appl. Phys. Vol.27 No.10, Oct 1988.

42) Masao Fukutomi et al; Japs J. Appl. Phys. Vol.27 No.8, Aug 1988 P 1484.

43) Ichiro Terasaki et al; Japs J. Appl. Phys. Vol.27 No.8, Aug 1988 P 1480.

44) Hidofumi Asano et al; Japs J. Appl. Phys. Vol.27 No.8, Aug 1988 P 1487.

45) Hisanori Yamane et al; Japs J. Appl. Phys. Vol.27 No.8, Aug 1988 P 1495.

46) Jadahiro Akune et al; Japs J. Appl. Phys. Vol.27 No.11, Nov 1988 P 2078.

47) Toshiro Marayama et al; Japs J. Appl. Phys. Vol.27 No.11, Nov 1988 P 2084.

48) Kiichi Yashiara et al; Japs J. Appl. Phys. Vol.27 No.8, Aug 1988 P 1492.

49) Kazuyuki Moriwaki et al; Japs J. Appl. Phys. Vol.27 No.11, Nov 1988 P 2075.

50) S.H. Pawar et al; Material Research Bull. Vol.27 No.7, P 642. 1990.

51) S.H. Pawar et al; Mat. Chem. and Phys. 28(1991), 259.

52) Komnik Y. Fu. et al; Soviet Phys. "Doklady" Englis Transl 5:072 (1960).

53) L. Bruke, Ann Physik 26:233(1936).

54) Manabe, T. and Other, Japs. J. Appl. Phys. 15 Sept 1991. V.30(9B), P L 1641.

55) Balkp et al; Trans. Met. Soc. AIME P. 563, (1965).