Chapter-6

MECHANICAL PROPERTIES OF PZT THIN FILMS

The nano indentation method is used to study the mechanical properties of thin films with high quality without removing the film from its substrate. The data obtained from nano indenter includes that of both substrate and film. This ambiguity is ruled over by an understanding of substrate effect which makes it clear about the contributions of both film and substrate. Because of charge considerations, the (100) orientation has the lowest surface energy and PZT nucleates heterogeneously at this orientation. At (100), the crystallites will be dominant due to fast growth kinetics [200]. In general, the mechanical properties of PZT thin films are calculated at this orientation in the present also they are focused at (100) orientation.

While measuring the mechanical properties of PZT thin films by nano indentation, the following procedure is considered:

- Based on one tenth ‘rule of thumb’, by considering the film thickness as a value less than 10 percent of original thickness and taking this as indentation depth the measured mechanical parameters resemble actual value of films [201].
- The micro cracks and accumulations should not be present in the films as the indentation depths of less than 20 % are possible [202].
- The young’s modulus is calculated from smooth places of load displacement curves where the values are constant and represent modulus of true films [203].

6.1 Mechanical properties of PZT films on different substrates

When many layers are there, the effect of the substrate is a summation of effects due to different layers during nano indentation measurement. For this, the measured values are always different even when an indenter penetrates in to the substrate [204].

The hardness varies as the indentation depth increases, this can be because of the occurrence of buckling and delamination in the PZT structures. Here there is no extensive propagation of interfacial cracks [205]. For complete fracture condition alone the effect of contact area play a role. But square root of change in contact area on young's modulus measurement is negligible when compared to the effect of the substrate.

When the indentation depth is higher than the supposed value the young' modulus varies as the elastic deformation continues to affect the substrate along with the film. This long range indentation depth implies its value on film properties also. [206].

In the present study, Nanoindentation analysis was used to study the mechanical properties of PZT thin films on alumina and quartz substrate as a function of sol temperature. The Berkovich indenter was used to make nine indentations for each sample; the given results are an average of these indentations. For all the samples the displacement- load curves have no discontinuities indicating the absence of cracks and delamination in the films.

The Young's Modulus (E_r) and the Hardness (H) of the films are calculated using the equations:

$$Young's\ Modulus\ E_r = \frac{\sqrt{\pi}}{2\beta}\frac{s}{\sqrt{A}}$$

Where s is stiffness, A=24.56 h^2 and β is shape constant of 1.034 for Berkovich Tip.

$$Hardness\ H = \frac{P_{max}}{A}$$

6.2 Mechanical properties of PZT thin films on Alumina substrate

The young's modulus and hardness were measured based on indentation depth for the PZT thin films on an alumina substrate, coated with sol at room temperature (SA1) and at 125^0C (SA2) are as shown in Fig. 6.1 & 6.2.

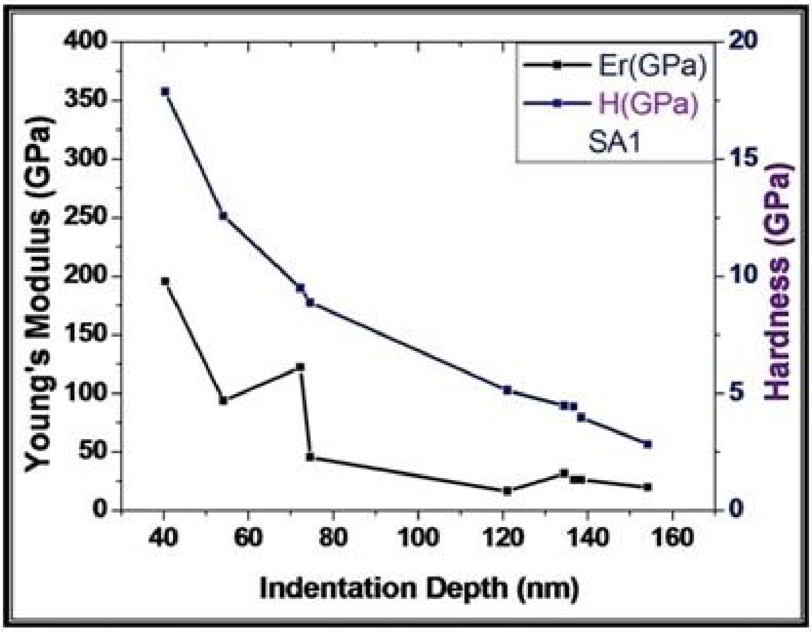

Fig. 6.1. Young's Modulus (E_r) and Hardness(H) Vs Indentation Depth for PZT Thin Film on Alumina Substrate (Room Temperature)

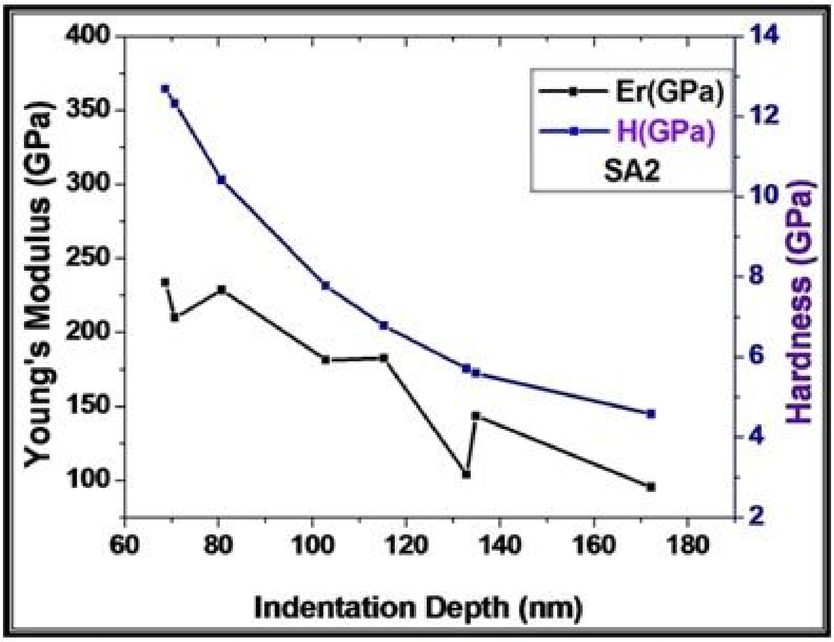

Fig. 6.2. Young's Modulus (Er) and Hardness(H) Vs Indentation Depth for PZT Thin Film on Alumina Substrate (125^0C)

By following the rule of thumb the indentation depth was taken as 10% of the thickness of the films. For SA1 film the thickness being 1.73 µm and for SA2 3.73µm, the indentation depth was less than 10% of these values. It was observed that with the rise in indentation depth the young's modulus and hardness decreased and the values match with the literature [207]. The PZT thin films were coated as 3 layers (SA1) and 2 layers (SA2) and in a multilayer system, the results are combined effect of layers and substrate. Here the SA1 film will have lower young's modulus compared to SA2 film which may be attributed to increase in grain size [208] with sol temperature. As the indentation depth increases the deformation of the substrate under the film increases and this provides an error in the values of mechanical properties. The hardness of the films is smaller as the film absorbs the layer with less applied strain compared to the films of high grain size.

The value of young's modulus in terms of film thickness and grain size for the PZT films on alumina substrate is shown in Table 6.1.

Table 6.1: Mechanical Parameters of PZT Thin Films
on Alumina Substrate with Sol at different temperatures

Sol Temperature	PZT Thin Film	Thickness µm	Grain Size nm	Young's Modulus (E_r) GPa	Hardness GPa
Room Temperature	SA1	1.73	30	117.7	9.2
125^0C	SA2	3.37	42	210.9	12.1

6.3 Mechanical properties of PZT thin films on quartz substrate

The young's modulus and hardness were calculated for PZT thin films on a quartz substrate in view of their thickness in nano ranges as 760nm (SQ1) and 955nm (SQ2) following the rule of thumb. With the indentation depth at less than 10% of thickness, the mechanical characterizations were as shown in Fig 6.3 & 6.4. For these films, the same effects of a decrease in young's modulus and hardness were observed with increase in indentation depth. But the observed values are less in view of the films on an alumina substrate. Here the effect of substrate on the type of coating is observed as the elastic deformation extends to the substrate even at small indentation depths [206].

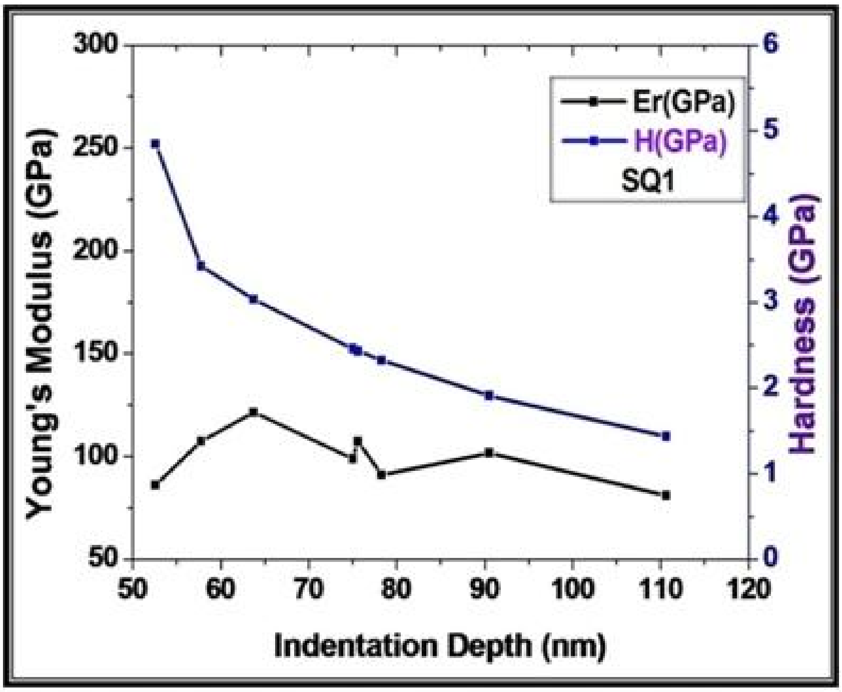

Fig. 6.3. Young's Modulus (E_r) and Hardness(H) Versus Indentation Depth for PZT Thin Film on Quartz Substrate (Room Temperature)

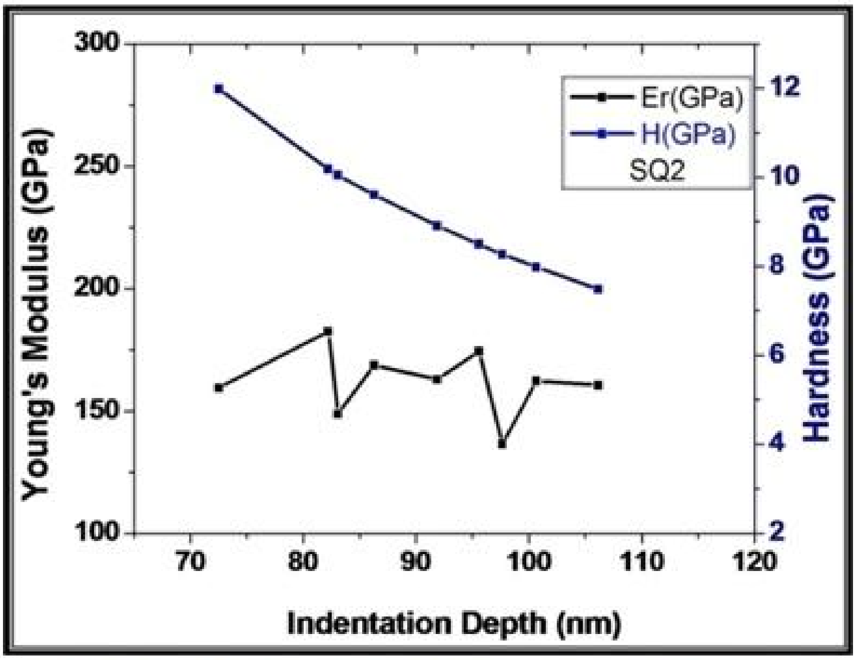

Fig. 6.4. Young's Modulus (E_r) and Hardness(H) Vs Indentation Depth for PZT Thin Film on Quartz Substrate (125^0C)

The hardness value of the PZT film is high in case of films with higher thickness, as it has internally confined plastic deformation. At lower thickness, the films are not able to stand the loads and deform with lower hardness. The hardness of the substrates is larger than the thin film in both cases and therefore the calculated hardness represents the real value of hardness of the thin film. In the present study, alumina served as a better substrate for mechanical properties of PZT thin films compared to quartz.

The results represent that the mechanical properties of PZT thin films are made better with the rise in sol temperature [207]. With high sol temperature the thickness of film increases, it provides minimal pores volume fraction and there by leads to diminution. Hence, the young’s modulus rises.

Nano indentation results indicate that the young’s modulus and hardness increases with an increase in grain size [209]. The values of young’s modulus and grain size as a function of film thickness and grain size for the PZT films on quartz substrates is shown in Table 6.2.

Table 6.2: Mechanical Parameters of PZT Thin Films on Quartz Substrate with Sol at different temperatures

Sol Temperature	PZT Thin Film	Thickness nm	Grain Size nm	Young’s Modulus (E_r) GPa	Hardness (H) GPa
Room Temperature	SQ1	765	24	86.8	4.9
125^0C	SQ2	945	27	159.3	11.9

The dependency of hardness on grain size is explained in terms of reverse Hall-Petch effect: the hardening material happens with an increase in grain size. The grain boundaries sliding is the main deformation process at these grain sizes and the regular dislocation-based deformation is not considerable in nano-crystalline materials with grain sizes less than 60nm [210]. The variation of mechanical parameters as a function of grain size for PZT thin films on alumina and quartz substrate are shown in Fig. 6.5 & 6.6.

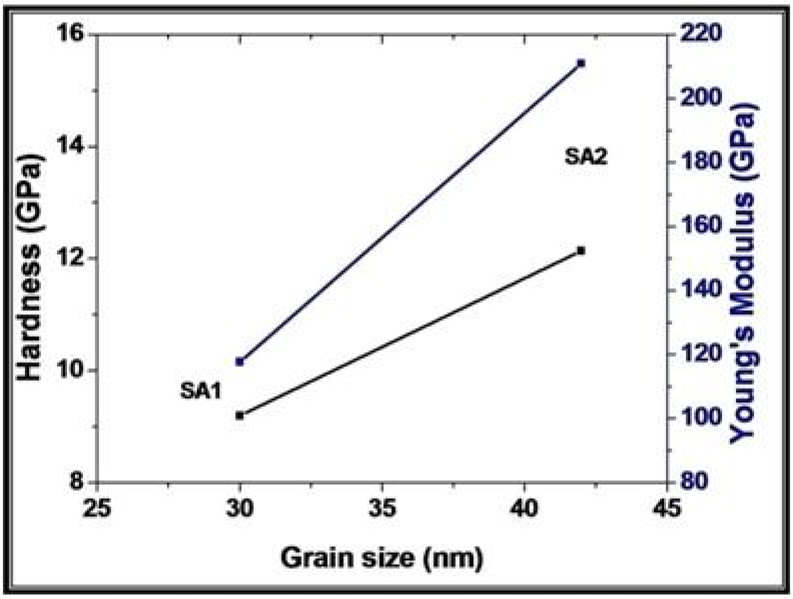

Fig. 6.5. Young's Modulus (E_r) and Hardness(H) Vs Grain Size for PZT Thin Film on Alumina Substrate

It is clear that for PZT thin films young's modulus increases from 117.7 GPa to 210.9 Gpa on an alumina substrate and from 86.8 GPa to 159.3 GPa on a quartz substrate. The hardness of PZT Thin Films varies from 9.2 GPa to 12.1 GPa on an alumina substrate. For quartz substrate, it varies from 4.9 GPa to 11.9 GPa.

In the present contest, the grain sizes of PZT thin films on both substrates are less than 45nm and the observed values of dislocation density and strain (Table 4.1) prove that the dislocation based deformation is not possible at these values. The hardness and young's modulus variations are assigned to grain boundary sliding and the grain sizes were dependent on sol temperature.

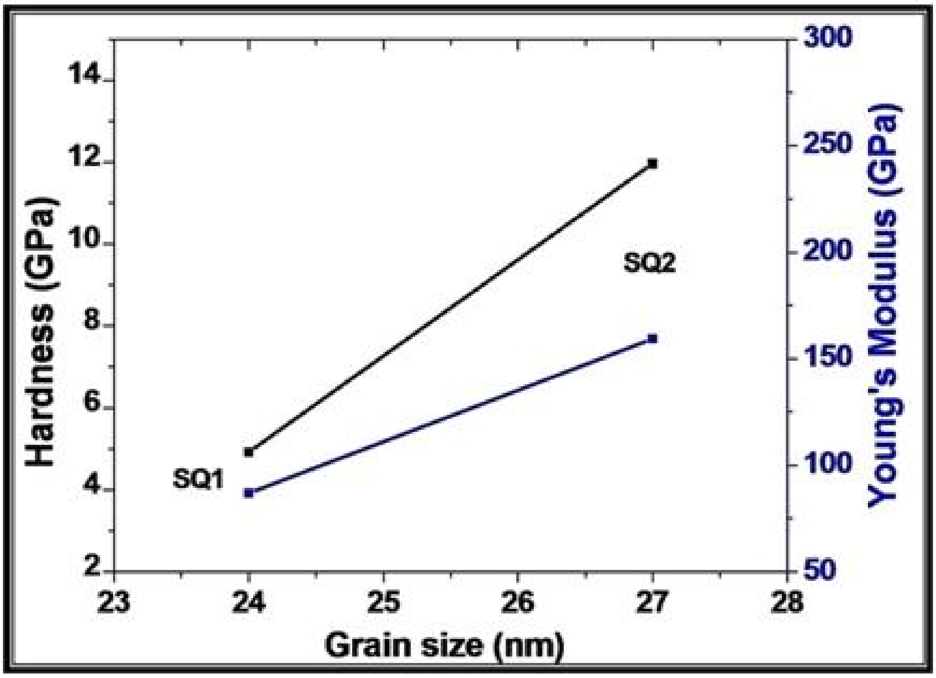

Fig. 6.6. Young's Modulus (E_r) and Hardness(H) Vs Grain Size for PZT Thin Film on Quartz Substrate

The variation of mechanical properties Young's Modulus and Hardness as a function of solution temperature is shown in the figures 6.7 and 6.8 for Alumina and Quartz substrates.

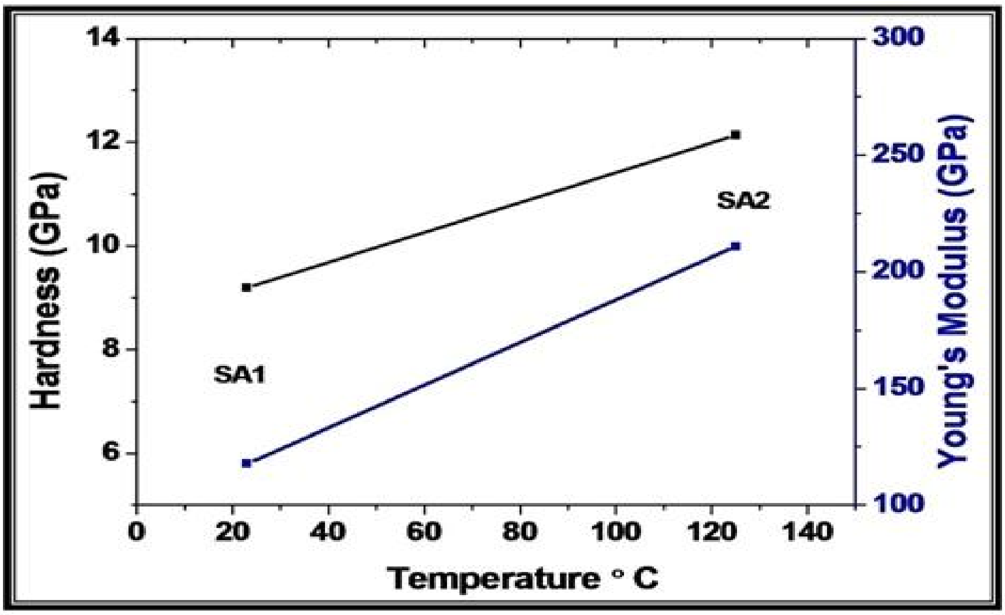

Fig. 6.7. Young's Modulus (E_r) and Hardness(H) Vs Solution Temperature for PZT Thin Film on Alumina Substrate

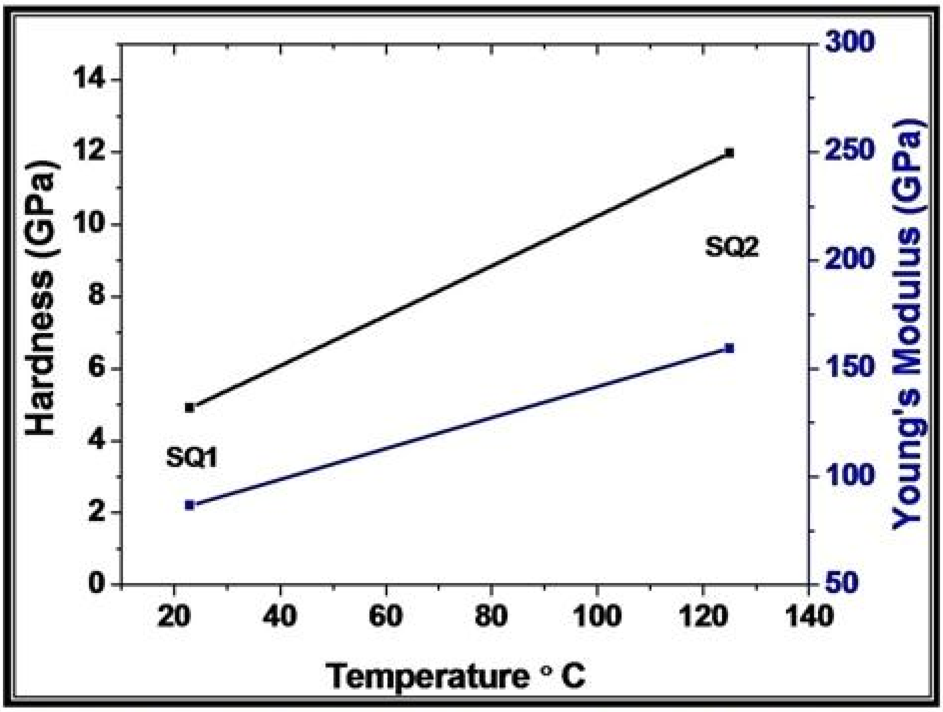

Fig. 6.8. Young's Modulus (E_r) and Hardness(H) Vs Solution Temperature for PZT Thin Film on Quartz Substrate

From the above discussion, it is clear that the mechanical properties of PZT thin films on both the substrates differ significantly. This variation can be attributed to synthesization and physical properties of thin films such as solution temperature, grain size, porosity, strain, thickness, type of substrate used. The experimental techniques adopted for studying the parameters are also a serious cause to scatter the mechanical properties.