MICROHARDNESS ANALYSIS IN AMORPHOUS As_2S_3 AND IN POLYCRYSTALLINE LiF AND NaF THIN FILMS USING DEPTH INDENTATION

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RESUMO

Neste trabalho são apresentadas medidas de microdureza efetuadas em filmes finos de As_2S_3 amorfo, e em LiF e NaF policristalinos. O método usado se baseia em ensaios de indentação dinâmica através da medida da penetração durante o carregamento. No caso de filmes finos a profundidade de penetração é da ordem de nanometros. A dureza para estes filmes é determinada em função de diferentes parâmetros experimentais.

ABSTRACT

In the present work microhardness measurements on amorphous As_2S_3 and on LiF and NaF polycrystalline thin films are presented. The method used is based on the submicron depth sensing indentation. The hardness is determined as a function of different experimental conditions as irradiation dose, film thickness and deposition temperature.

1. INTRODUCTION

The analysis of the mechanical behavior of thin films become very important in recent years because the increasing use of new optoelectronic integrated devices. The mechanical properties of the materials, deposited in form of thin films, are strictly correlated with the performance of the related system.
Amorphous chalcogenides glasses and polycrystalline alkali fluorides thin films have been studied with renewed attention since their characteristics allow possible application in new photonic devices[1,2]. Within the chalcogenides, the amorphous arsenic trisulfide (a-As_2S_3) is one of the most investigated, due to the structural transformations undergone when it is exposed to a radiation source[3]. Moreover, technological application may take advantage of the optical properties of lithium fluoride (LiF) and sodium fluoride (NaF) as single and multilayer films, which can host high densities of several active defects produced by ionizing radiations[4].
The measurement of mechanical properties of a material through depth sensing indentation tests has become common for thin films[5,6,7,8]. This technique, known as dynamic indentation test, gives information about the displacement of the indenter as a function of the applied load during the measuring process.
In present work, the microhardness and the modulus of elasticity of amorphous As_2S_3 films deposited onto glass and Si(100) substrates, under different illumination doses are determined. The same measurements were also performed for polycrystalline LiF and NaF thin films grown at different temperatures. The influence of the substrate on the film properties was also investigated and taken into account for all these materials. With this purpose the hardness measurements were done for samples with different thickness, from 0.7 to 4 μm.

2. EXPERIMENTAL AND METHODS

2.1 Film Deposition and Irradiation

The a-As_2S_3 and the fluorides films were grown by thermal evaporation and electron beam techniques respectively, in a high vacuum chamber. The deposition rate was 1.5 nm/s for a-As_2S_3 and 1.0 nm/s for LiF and NaF. The thickness of the deposited films were confirmed by further measurements performed with a profilometer. Optical glass and Si(100) were utilized as substrates. During the deposition process, the temperature of substrates was kept constant by using a PID controller.
The irradiation of the a-As_2S_3 films was performed with an infrared filtered Hg-Xe high power lamp. The measured power density on the samples was about $65 mW/cm^2$, and different doses were obtained by exposing them during different times.

2.2 Hardness Measurements

The film indentation were performed in a microhardness equipment Fischer HV 100. This instrument provides data about the load and the displacement during the indentation, with a load range spanning from 1 mN to 1 N. In our experiments a maximum load of 3 mN was applied to the samples to avoid undesired substrate influence. The hardness represents the mean pressure on the indenter during the indentation and can be expressed as:

$$HV = \frac{Q}{A} \qquad (1)$$

where Q is the applied load and A is the projected contact area. After the indentation test, a curve of load against

depth is provided; an example of such curve is shown in Fig. 1. From this curve the hardness under load (HU) and the plastic hardness (HP) are calculated by the equipment software. In particular the HP value is calculated through the slope of a straight line tangent to the point of the maximum load. There is not a direct proportionality between the HP and the Vickers hardness values, principally because the HP doesn't take into account the material elastic response. Moreover, the elastic recovery of the material (We) and the modulus of elasticity (E) are also provided by the equipment. The load F is applied through a potential law, default of the instrument, following the equation:

$$\frac{d\sqrt{F}}{dt} = cte. \qquad (2)$$

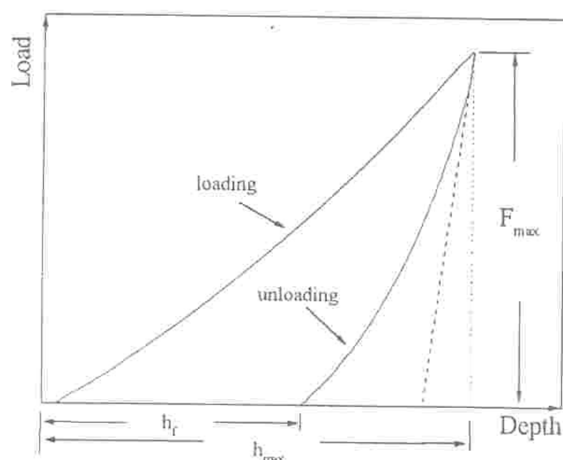

Figure 1 – An example of the curve of the load against the depth obtained in a depth sensing indentation test. F_{max} is the maximum applied load; h_f is the final depth; h_{max} is the maximum depth reached under load.

3. RESULTS AND DISCUSSION

The results and analysis of the samples hardness as a function of the film thickness, the irradiation dose and the deposition temperature will be presented and discussed.

3.1 Thickness Dependence

In the case of a-As_2S_3 films, samples with thickness from 0.7 to 2.5 μm do not presented a remarkable difference in their hardness values, as shown in figure 2. From the above results it is evident that the substrate is not affecting the hardness measurements in the film thickness range. So, the HP value for the non-irradiated a-As_2S_3 films can be estimated in about 890 N/mm^2.

For the polycrystalline LiF and NaF films, deposited onto glass and Si(100) substrates, a similar analysis was performed. In this case the thickness values changed from 1 to 4 μm. The results are shown in figures 3(a) for LiF and 3(b) for NaF respectively. The hardness of both materials seem to present a dependence with the film thickness, with a more pronounced one for the NaF specimen. A possible explanation could be found in the different film growth structure, as a preliminary scanning electron microscopy (SEM) analysis has suggested.

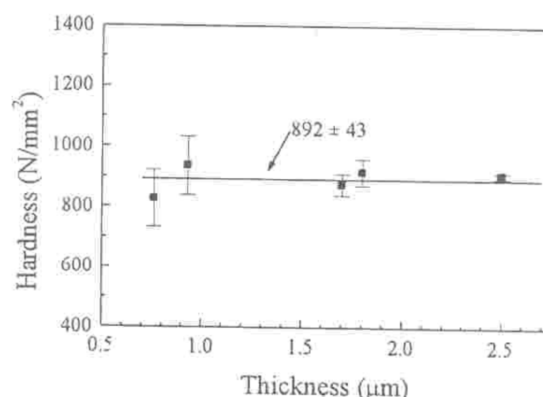

Figure 2 - Plastic hardness, HP, as a function of a-As_2S_3 film thickness. The HP mean value is also indicated.

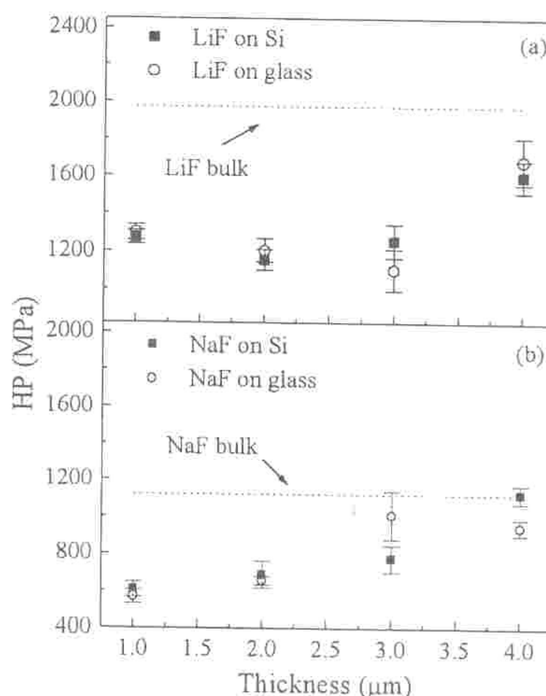

Figure 3 - Plastic hardness, HP, as a function of film thickness for LiF (a) and NaF (b). The film and bulk HP mean values are also indicated.

Furthermore, it was found that as the thickness increases, the indentation test can induce a lost of adhesion of the film to respect to the substrate. In this way, the hardness of the substrate begin to be prevailing. This effect is more evident for the NaF films thicker than 3 μm. Taking into account these considerations, a hardness mean value of the

order of 1200 N/mm^2 for LiF films and of about 650 N/mm^2 for NaF films can be estimated.

3.2 Irradiation

Some a-As_2S_3 samples were irradiated as described in section 2.1 to study the relation between the hardness with the different irradiation doses. These measurements can give useful information about the influence of the irradiation dose on the structural transformation undergone by this material. In figure 4 the related results are presented.

From the experimental data the hardness seems to increase until reach a saturation value. This behavior can be due to the co-existence of different kind of chemical bonds (As-S, S-S and As-As) in the non irradiated films. During the illumination the homopolar bonds are broken and energetically more favorable heteropolar bonds are formed instead, making the film more continuos and therefore harder[3].

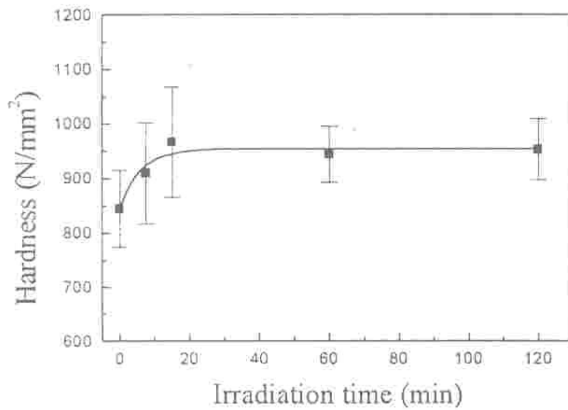

Figure 4 - Plastic hardness variation of a-As_2S_3 films as a function of the irradiation time (scattered points). The full line is a best fit curve obtained using the equation $h \sim (1\text{-}\exp(-t/\tau))$, where τ is a characteristic time of the process.

3.3 Deposition Temperature

Polycrystalline LiF and NaF thin films experience a change in their structural and morphological characteristics when grown at different temperatures, as already observed elsewhere[9,10]. Keep in mind this fact, become relevant an investigation of the relation between the hardness and the film deposition temperature. In our experiment during the evaporation process, the substrate temperature was kept constant at 50, 100 and 200°C and with the temperature controller connected to the system it was possible to regulate the cooling rate after each deposition. In figure 6 the experimental data are reported together with their best fit, obtained using a simple mathematical expression with a saturation trend.

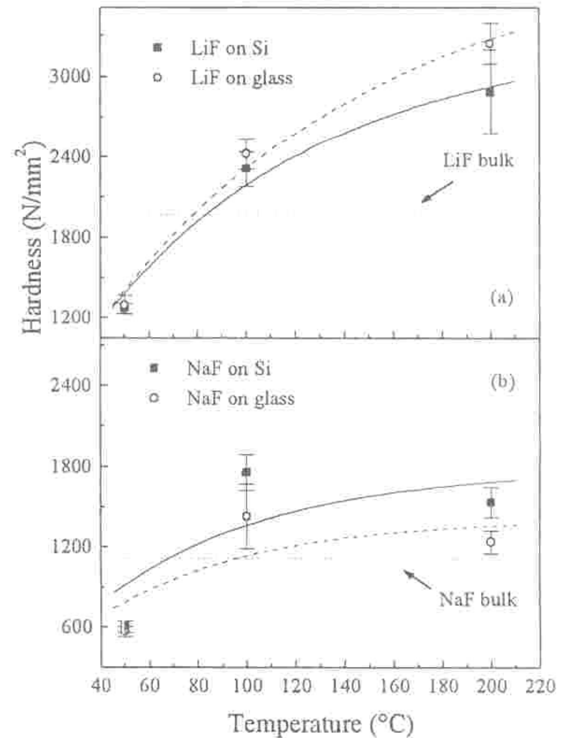

Figure 6 - Plastic hardness, HP, as a function of film deposition temperature for LiF (a) and NaF (b). The bulk HP mean values are also indicated.

For both the alkali fluorides, the plastic hardness values increase with the deposition temperature and they seem to present a saturation trend. This behavior, which can be explained by the increase of the grain size with the temperature presents in LiF and NaF thin films[9,10], is almost independent of the chosen substrate. Also, only after 100°C the hardness of the two materials become higher than the respective bulk values (dotted lines in Fig.6). The reason could be found in a dependence of the crystallite orientation with respect the deposition temperature[9].

3.4 Elasticity Modulus

The microindenter equipment software also provides the values of the elasticity modulus, E, obtained from the loading and unloading data. In Table I the values of E for a-As_2S_3, LiF and NaF films deposited on Si(100) are reported for different experimental conditions.

Table I - E values of the different analyzed films

Film	Exp. Condition	E (GPa)
a-As_2S_3	non-irradiated	20
a-As_2S_3	120 min irradiated	22
LiF	50°C deposited	87
LiF	200°C deposited	120
NaF	50°C deposited	49
NaF	200°C deposited	82

4. CONCLUSION

Microhardness measurements of a-As_2S_3, LiF and NaF thin films were achieved using a dynamical indentation method. From the same set of data, the values of the elasticity modulus for these films were also attained.

Although these measurements are very useful for the determination of the mechanical properties of thin films, the hardness data obtained by the depth sensing indentation method and the conventional Vickers one are different mechanical tests, and their values are not comparable. Nevertheless in this work we was able to obtain for the first time a preliminary quantitative hardness results for two classes (dielectric and semiconductor) of materials in form of films. In spite of the results show a certain behavior as a function of various experimental parameters (irradiation dose, film thickness and deposition temperature) the errors associated to the method should be reduced. For this reason further investigation are carried on the same materials.

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