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Oxidation temperature and vapor chopping effects on superficial properties of Bi_2O_3 thin film prepared on glass and alumina substrates

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ABSTRACT

The nanoscale bismuth oxide thin films prepared by thermal oxidation (in air) of vacuum evaporated vapor chopped and nonchopped bismuth metal thin films on crystalline alumina and amorphous glass substrates. The effect of substrate nature on the structural, surface morphological, contact angle, electrical resistivity and adhesion properties of Bi_2O_3 thin films were studied. It is found that the substrate effect was prominently manifested in the surface morphology. Effect of oxidation temperature on thin films properties was also investigated. The surface roughness of deposited Bi_2O_3 thin films were found to increase on glass while it reduced on alumina with increase in oxidation temperatures. All the films showed hydrophilic nature. Contact angle was found to decrease with increase in surface roughness in all cases. Adhesion, crystallinity and grain size of bismuth oxide films on alumina substrate was found to be higher than in the case of Bi_2O_3 thin films deposited on glass. Vapor chopped thin films showed higher adhesion, smaller grain size, higher contact angle, lower resistivity and smooth surface morphology.

Keywords: Oxides, thin films, Vapor deposition, X-ray diffraction, Mechanical properties, Surface morphology.

INTRODUCTION

Bismuth oxide is an interesting material characterized by significant band gap, resistivity and dielectric permittivity [1]. Bismuth oxide thin films have diverse applications ranging from radio to optical frequency range of the electromagnetic spectrum. The substrate plays a very important role for the suitable application of the thin film. If integration of optical device with radio frequency /microwave device is to be made, it is essential that the effect of substrate properties on deposited thin film have to known. Generally the effect of substrate surface roughness is a pre-considered aspect and tends to be neglected. To study substrate variation effect on deposited thin film properties, polycrystalline alumina (Al_2O_3) and amorphous glass substrates have been used in this work. They are extensively used in advanced technology for optoelectronic and high radiofrequency range applications as they fulfill most of the general requirements for a good substrate material. The preparation methods and conditions can strongly influence the properties of bismuth oxide thin film [2-5].

Vapor chopping technique (with substrate at room temperature) developed at our laboratory has been reported to improve the mechanical and optical properties of thin film coatings on glass substrate [6, 7]. Adhesion of bismuth oxide thin film on glass substrate has been previously reported by us [8, 9]. But no reports were published so far on the adhesion and other surface properties of bismuth oxide thin films deposited on alumina substrate.

In this present paper the structural properties, electrical resistivity, surface morphology, surface roughness, contact angle and adhesion of Bi_2O_3 thin films on alumina and glass were studied and the effect of vapor chopping on these properties was investigated. Though the adhesion and structural properties of Bi_2O_3 thin films on glass and the effect of vapor chopping has been reported in refs [8, 9], but the effect of vapor chopping on the surface roughness, electrical resistivity and contact angle of Bi_2O_3 thin films deposited on alumina substrate are being reported for first time here.

MATERIALS AND METHODS

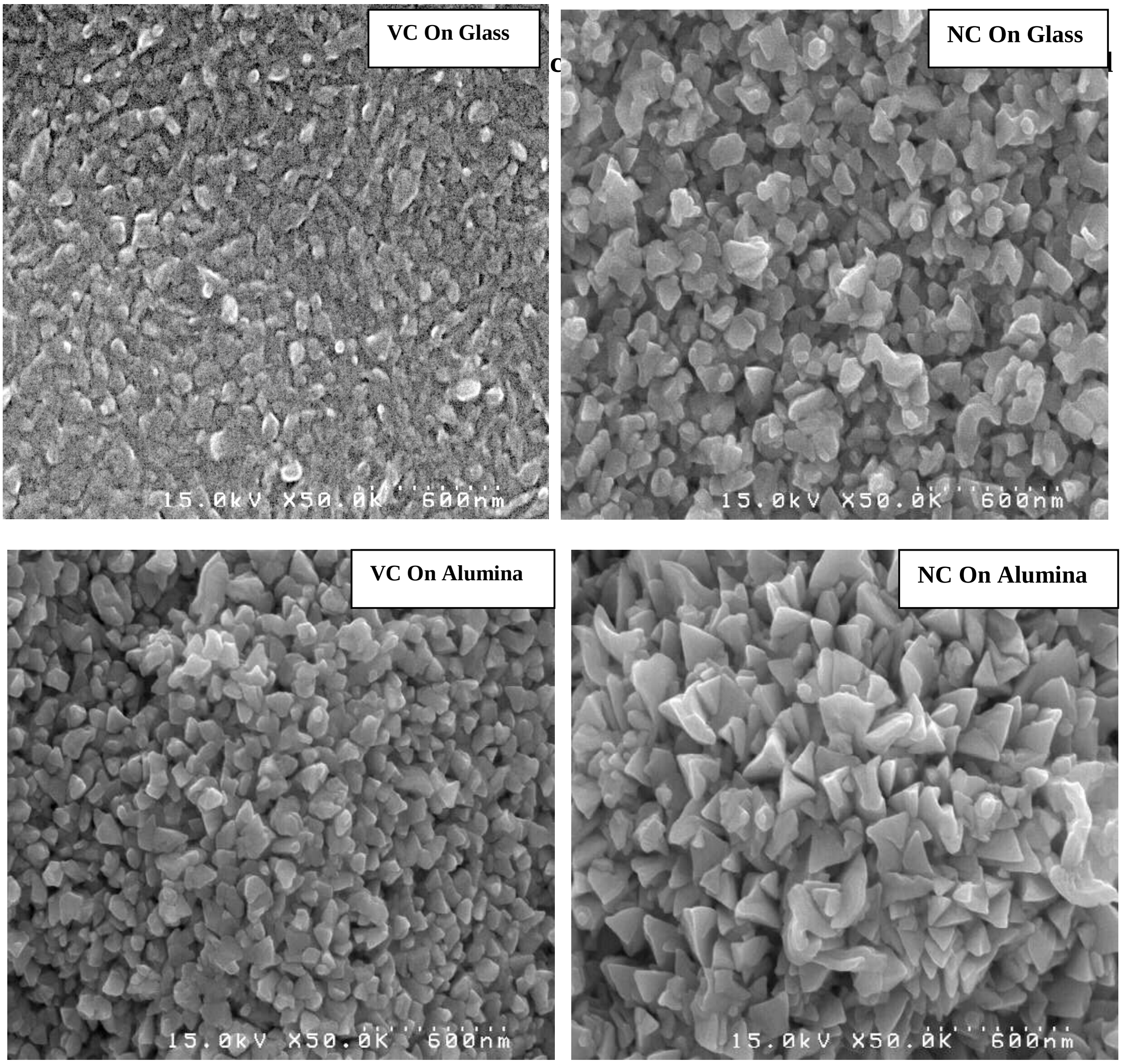
Bismuth thin films have been prepared by vacuum (10^{-5} mbar) evaporation at room temperature onto alumina and glass substrates by using a molybdenum boat. The pure (99.7 %) metallic bismuth (Balzers) was used as the source material. Deposition of Bi_2O_3 on glass substrate by this technique has been previously reported [8,9]. Vapor chopping technique is described in ref [7]. Bismuth oxide thin films were obtained by thermal oxidation (in air) of nonchopped and vapor chopped bismuth films at different oxidation temperatures (423, 473 and 523K) for 10 min duration. The thickness of the films was 200nm, as measured by Tolansky interferometric method. The structural analysis by X-ray diffraction (XRD) was carried out on a Philips PW 3710 diffractometer and surface morphology was inspected by Field Emission Scanning Electron Microscopy (FESEM), using a SEMHITACHI S-4100 MODEL system. The DC electrical resistivity of bismuth oxide thin films was measured as a function of temperature in the range 300-623 K by using two-probe method. The surface roughness was measured by XP-1 surface profiler (AMBIOS Technology) and contact angle by using contact angle goniometer (Ramehart instruments company USA). Adhesion was measured by direct pull-off (DPO) method [6,7].

RESULTS AND DISCUSSION

3.1 Structural

Fig.1 shows XRD patterns of bismuth oxide a) vapor chopped b) nonchopped thin film on alumina. It was observed that monoclinic Bi_2O_3 and δ- Bi_2O_3 are predominant phases in all above cases. The bismuth oxide films on glass substrate deposited by same method have also shown predominance of monoclinic Bi_2O_3 and δ- Bi_2O_3 as previously reported [8,9]. Bi_2O_3 thin film deposited on alumina substrate showed the strong γ- Bi_2O_3 (BCC) reflection. The presence of β- Bi_2O_3 phase was found in nonchopped bismuth oxide thin film deposited on alumina which was absent in the vapor chopped films. BiO phase was observed in vapor chopped and nonchopped Bi_2O_3 films deposited on alumina substrate.

We mention that the peak intensity of Bi_2O_3 thin films deposited on alumina substrate was higher than that reported for Bi_2O_3 thin film deposited on glass [8, 9]. It is attributed to the higher crystallinity of the alumina substrate as compared to glass. XRD pattern of Bi_2O_3 film deposited on glass [8, 9] consists of more noise due to the amorphous structure of glass substrate whereas noiseless pattern was obtained of Bi_2O_3 thin films on crystalline alumina substrate. Fig. 1 inset shows the XRD pattern, of the bare alumina substrate.



3.2 Surface morphology

Figure 2 depicts FESEM micrographs of vapor chopped and nonchopped bismuth oxide thin films onto both glass and alumina substrates, prepared by thermal oxidation at 423 K. It was observed that, the grain growth was predominantly substrates (glass and alumina) dependent. Surface morphology of films on glass substrate was found to be smoother than in the case of alumina substrate. The vapor chopping effect on the Bi_2O_3 thin film deposition was clearly observed in grain structure. The vapor chopped Bi_2O_3 thin films displays better surface morphology, smaller grain size and less defects (voids, cracks) as compare to the nonchopped thin films.

Vapor chopped Bi_2O_3 thin films on glass showed flat, platy irregular shaped nanongrains structure with clusters, whereas nonchopped Bi_2O_3 thin films showed randomly oriented grains having comparatively lesser clustering behaviour. The nonchopped thin films showed grain size of ~25 nm whereas it was ~15 nm in vapor chopped Bi_2O_3 thin films deposited on glass. The vapor chopped Bi_2O_3 thin films deposited on alumina substrates showed highly agglomerated irregularly shaped granular structure whereas nonchopped thin film showed novel triangular-shaped cauliflower grain structure (obtained for the first time in vacuum evaporated Bi_2O_3 thin films). The size of triangular shaped grains size of ~70- 90 nm in NC Bi_2O_3 thin films, whereas it reduces up to ~ 40 nm in VC Bi_2O_3 films on alumina.

From FESEM images (fig. 2) of Bi_2O_3 thin films deposited on glass as well as alumina substrates observation, it was found that thin films deposited on glass showed a planar grain growth, whereas those on alumina substrates display a hump-like growth nature. This fact emphasizes the influence of substrate crystallinity and roughness on deposited thin films.

3.3 Surface roughness

The surface roughness (at room temperature) of crystalline alumina substrate (608 nm) was higher as compared to amorphous glass substrate (13nm). Table 1 shows that, bismuth thin film deposited on alumina has higher surface roughness than the film deposited on glass. Low roughness of glass substrate (13 nm) enables formation of most of the nanoparticles in a given x-y plane [10] with less point defects. However, higher substrate roughness of alumina, reduces the number of nanoparticles aligning in a given x-y plane. Deposition of thin film on rough surface provides point defects due to the formation of voids trapped between rough substrate surface and deposited thin film.

Table 1. Surface roughness of vapor chopped and nonchopped bismuth and bismuth oxide thin films on alumina and glass substrate.

Material	Temperature (K)	Surface roughness (nm)			
		Alumina substrate		Glass substrate	
		VC	NC	VC	NC
Bismuth film	Room temp.	1013	1291	38	81
Bismuth oxide film	423	976	1002	51	180
	473	711	836	96	296
	523	650	684	134	506

Table 1 shows that, the surface roughness of Bi_2O_3 thin film on glass increases with oxidation temperature whereas it decreases in the case of Bi_2O_3 thin film on alumina. The surface roughness varies during oxidation, it was found to depend on the kinetics of grain growth process and reduction in point defects of thin film. As the oxidation temperature increases, the surface roughness increases due to films crystallization and the huge grain growth with drastic grain agglomeration [11-13] whereas it reduces with decrease in film's point defects with decrease in its dislocation density [14]. If more point defects are available, the oxygen atoms can work together to form the substrate-film interface and suit the adatoms best with substrate. If point defects are not available, then the ability of the adsorbed oxygen to cooperate is reduced [15] due to which surface roughness increases.

From table 1 it was found that, the Bi_2O_3 thin film deposited on both alumina and glass substrates, the surface roughness of vapor chopped Bi_2O_3 thin films were lower than the nonchopped Bi_2O_3 thin films. The effect is more pronounced in the film on glass. Grain growth of vapor chopped thin films was slower and smaller in grain size than the nonchopped Bi_2O_3 thin films. Vapor chopping technique provides more residential time for the adatoms to settle on the substrate; it affects the nucleation kinetics during film growth and helps to reduce the point defects during the deposition of bismuth thin films.

3.4 Contact angle

From figure 3 it is seen that, the Bi_2O_3 thin films deposited on both alumina and glass substrates are hydrophilic in nature. Contact angle of Bi_2O_3 thin films deposited on the glass substrate is greater than that of Bi_2O_3 on alumina, might be due to higher surface roughness obtained for the bismuth oxide thin film on alumina. The contact angle of Bi_2O_3 deposited on glass increases with oxidation temperature, whereas for the film deposited on alumina the contact angle decreases with increase in oxidation temperature. The surface roughness of the Bi_2O_3 thin films on glass increases due to increase in oxidation temperature due to which the contact angle also increases with oxidation temperature.

Vapor chopped Bi_2O_3 thin films show higher contact angle than the nonchopped thin films deposited on alumina and glass substrates. Observation of FESEM images supports that surface roughness of vapor chopped thin film is lesser than that of nonchopped thin films.

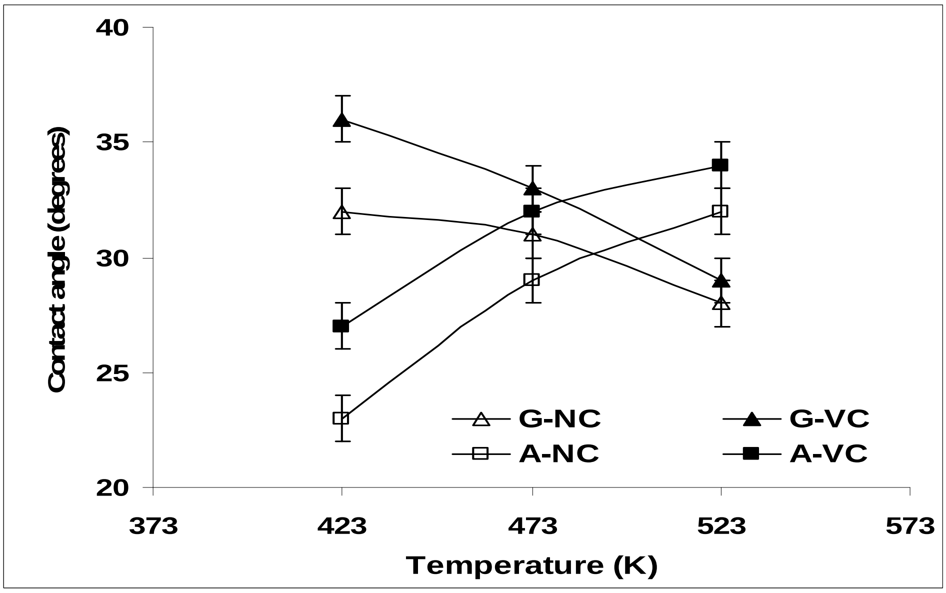


Fig. 3. Temperature dependence of contact angle of vapor chopped and nonchopped Bi_2O_3 thin films deposited on alumina (A) and glass (G) substrate

3.5 Electrical Resistivity

Figure 4 shows the variation of DC electrical resistivity of bismuth oxide thin film of a) vapor chopped b) nonchopped on glass substrate and c) vapor chopped d) nonchopped on alumina substrate respectively oxidized at different temperatures (423 K, 473K and 523K) measured as a function of temperature in the range 300-623 K. Electrical resistivity of bismuth oxide films, at the room temperature, was found to be the order of 10^5 Ωcm. The graph showed that the electrical resistivity of Bi_2O_3 films deposited on glass was lower than that of films on alumina. The nonchopped Bi_2O_3 thin films deposited on alumina showed higher resistivity of the order of $10^8 \Omega$cm than the vapor chopped ~10^5 Ωcm, whereas it was ~10^7 Ωcm for nonchopped and 10^5 Ωcm for vapor chopped films on glass. Oxidation temperature dependent effects are more prominent when alumina was used as substrate.

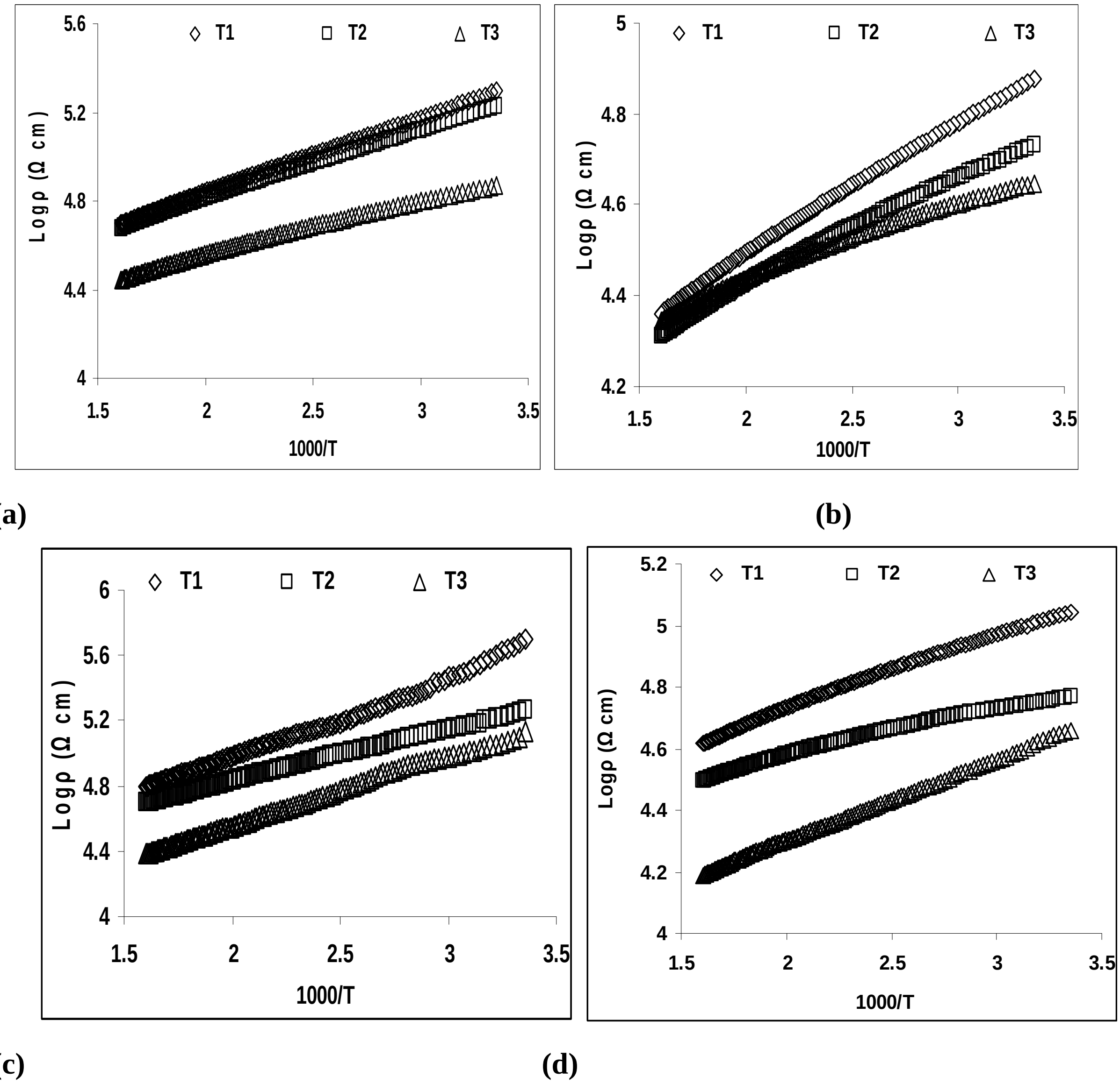


Fig. 4: Temperature dependence of DC electrical resistivity of vapor chopped (a) and nonchopped (b) bismuth oxide films on glass substrate and alumina substrate (c) and (d), respectively. Oxidation temperature: T1=423 K, T2=473 K and T3=523 K

The electrical resistivity of polycrystalline material is expected to be higher than that in the case of corresponding nanocrystalline materials [16]. The results obtained from the DC resistivity measurements have good agreement with thin films surface morphology. It was found that, increase in grain size causes the resistivity enhancement i. e. as grain size decreases electric resistivity reduces linearly. Nonchopped Bi_2O_3 thin films showed maximum resistivity on alumina substrate, which decreases in the case of VC thin films. The vapor chopped Bi_2O_3 thin films on glass display compact structure and smaller grain size as well as lower electrical resistivity. The effect of increase in oxidation temperature is to decrease the resistivity for both the vapor chopped and nonchopped films.

3.6 Adhesion

The adhesion of bismuth oxide thin films on glass substrates for higher temperature have has been previously reported, it was found to be in the range 215 – 470 x 10^2 kgF/cm^2 [8] for different oxidation duration and thickness. Increase in adhesion due to increase in oxidation temperature was observed in the Bi_2O_3 thin film deposited on both alumina and glass substrate. Fig. 5 shows adhesion of vapor chopped and nonchopped bismuth oxide thin films deposited on alumina (A) and glass (G) substrate at different oxidation temperatures. The adhesion of bismuth oxide films on alumina substrate was found to be quite higher than for Bi_2O_3 on glass. The improvement in crystallinity of the Bi_2O_3 thin films causes the increase in adhesion. The quality of adhesion depends to a large extent on the interface layer formed between the substrate and film due to existence of transition region.

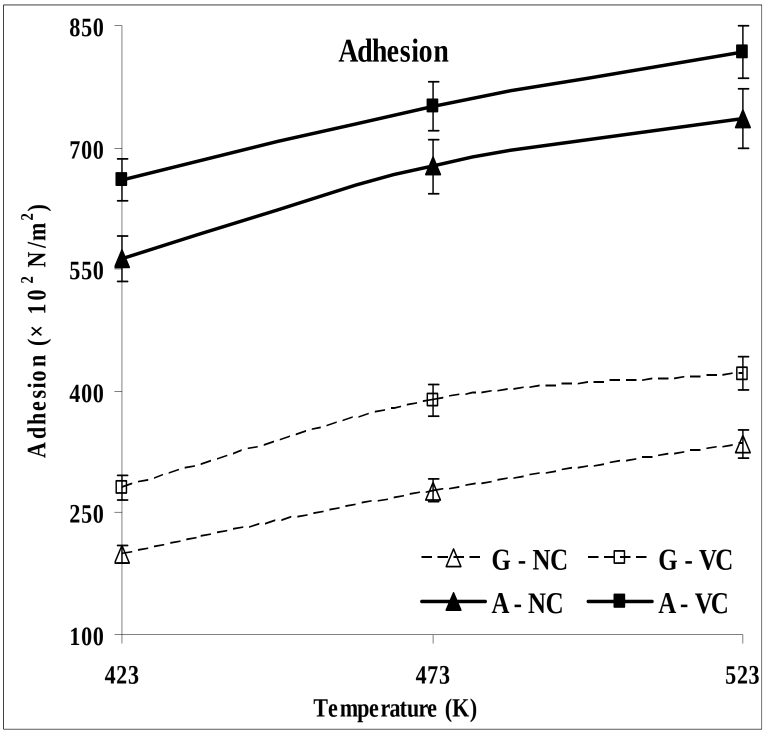


Fig. 5: Adhesion of vapor chopped and nonchopped bismuth oxide thin films deposited on alumina (A) and glass (G) substrate.

The adhesion of vapor chopped bismuth oxide thin film on alumina was in the range 660 - 818 x 10^2 kgF/cm^2 whereas that of nonchopped bismuth oxide thin films was in 573 - 735 x 10^2 kgF/cm^2 range. The difference in the adhesion of nonchopped and vapor chopped films is much larger than the experimental error (9.8 kgF/cm^2), which allows us to conclude that the vapor chopping increases the adhesion of the Bi_2O_3 thin film on alumina also.

Good adhesion is promoted by low stress and non-planar defects and low concentration of flaws. Generally, during the evaporation process, the solid material turns into vapor form. The evaporated atoms (adatoms) acquires the kinetic energy, these adatoms may or may not be completely thermally equilibrate. When adatoms arrive closer to substrate, they moves horizontally over the substrate surface by jumping from one potential well to the other because of thermal activation from the surface and /or its own kinetic energy parallel to the surface. The adatoms has finite residence time on the surface during which they may interact with other adatoms to form a stable cluster [17]. Due to continuous arrival of adatoms, columnar growth of the film takes place and number of void increases. The vapor chopper used in vapor chopping technique interrupts the vapor flow during the evaporation process before the condensation on the substrate with constant rate which give a certain residence time to the previously evaporated adatoms to settle completely at minimum energy potential well. This helps to create new nucleation centers and helps to minimize the columnar growth and form an uniform dense thin films. The improved surface morphology and reduced columnar structure, cracks and voids formation in MgO thin films by using vapor chopping technique were observed by taking cross section SEM micrographs, as was earlier reported [18]. The rougher surface of alumina substrate provides larger contact points between thin films and substrate, resulting in increase in adhesion of the thin film.

CONCLUSION

Highly adhesive polycrystalline bismuth oxide thin films on alumina substrates have been deposited by thermal oxidation in air of vacuum evaporated Bi thin films. The thin film-substrate interface has great importance in nanoscale material deposition using thin film technology. Surface roughness, used substrate and oxidation temperature are the responsible factors for variation in superficial properties i. e. crystal structure, surface morphology, electrical resistivity, contact angle and adhesion of Bi_2O_3 thin films. It was found that these superficial properties are interrelated with each other. Substrate roughness and temperature variation affect the thin film surface roughness. Increase in roughness decreases the contact angle. The grain size of the bismuth oxide thin film drastically increases when it is deposited on alumina substrate. Adhesion of Bi_2O_3 thin films on alumina was found to be higher than that of the films on glass. Due to the vapor chopping technique, there seems to be a voids and other imperfections reduction in vapor chopped thin films compared to the nonchopped during thin film growth, it resulting in modification in Bi_2O_3thin films superficial properties.

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