UDK 546.87:620.179.11
Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 39(1–2)25(2005)

SINTEZA TANKIH PLASTI $Bi_{12}SiO_{20}$ Z METODO SOL-GEL

THE SYNTHESIS OF $Bi_{12}SiO_{20}$-BASED THIN FILMS BY THE SOL-GEL METHOD

Asja Veber, Matjaž Valant, Danilo Suvorov

Institut "Jožef Stefan", Odsek za raziskave sodobnih materialov, Jamova 39, 1000 Ljubljana, Slovenija
Asja.Tajnsek@ijs.si

Prejem rokopisa – received: 2004-10-04; sprejem za objavo – accepted for publication: 2005-03-07

The phase formation and microstructural development of $Bi_{12}SiO_{20}$ thin films prepared on a sapphire substrate using the sol-gel method have been investigated. For the deposition of the thin films from the precursor solution we used the dip-coating method with a withdrawal speed of 15 cm/min. A homogeneous and stable solution was obtained from $Bi(NO_3)_3.5H_2O$ and $Si(OC_2H_5)_4$ (TEOS). The stability of the solution was determined by its concentration, which directly affects the microstructure. The films were annealed in the temperature range from 300 °C to 700 °C. Single-phase $Bi_{12}SiO_{20}$ polycrystalline thin films were formed at a temperature between 600 °C and 700 °C. After drying and densification, these films were characterized using X-ray diffraction (XRD) and scanning electron microscopy.

Key words: $Bi_{12}SiO_{20}$, thin films, sol-gel method, dip-coating technique

Fazne transformacije in razvoj mikrostrukture tankih plasti $Bi_{12}SiO_{20}$ na safirjevi podlagi, ki so bile pripravljene z metodo sol-gel, so opisane v tem prispeku. Tanke plasti smo pripravili s tehniko potapljanja pri konstantni hitrosti 15 cm/min. Homogeni stabilni sol smo pripravili s prekurzorji $Bi(NO_3)_3.5H_2O$ in $Si(OC_2H_5)_4$. Stabilnost sol-a je bila določena s koncentracijo, ki neposredno vpliva na mikrostrukturo tanke plasti, ki so bile žgane pri temperaturah od 300 °C do 700 °C. Eno fazno polikristalinično tanko plast $Bi_{12}SiO_{20}$ smo dobili pri temperaturi med 600 °C in 700 °C. Po sušenju in žganju so bile tanke plasti karakterizirane z rentgensko praškovno analizo (XRD) in vrstično elektronsko mikroskopijo (SEM).

Ključne besede: $Bi_{12}SiO_{20}$, tanke plasti, sol-gel, tehnika potapljanja

1 INTRODUCTION

Bismuth silicon oxide, $Bi_{12}SiO_{20}$ (BSO), which has a sillenite structure, is a piezoelectric, electro-optic, photo-refractive and optically active material. It also exhibits strong photoconductivity in the near-ultraviolet spectral range [1]. Recently, sillenites have begun to be considered for use as dielectrics in the field of electronics [2]. They are used as a new material in LTCC (Low-Temperature Cofired Ceramic) technology because of their good chemical and dielectric properties. A characteristic of LTCC technology is cofiring the multilayer structure at low temperature, and therefore it is very important that the dielectric layer of BSO is compatible with the electrode, and that it has a lower sintering temperature than the melting point of the electrode [3]. The advances in communications technology observed in the past 10 years have been supported by the development of new materials that enable miniaturization. Because of the good chemical and dielectric properties of BSO we decided to prepare thin films of this material using the sol-gel method. Thin films of BSO have already been prepared by Chemical Vapour Deposition (CVD) [4] and the sol-gel process [1,5]. The sol-gel process allows the synthesizing of ceramic materials with a high homogeneity, since the alkoxides are mixed at the molecular level in the solution. The cations of different types are uniformly distributed on an atomic scale through M-O-M bridges. However, a major problem in forming a homogeneous multi-component solution is the unequal hydrolysis and condensation rates of the metal alkoxide. This can result in phase separation, during the hydrolysis or thermal treatment, leading to higher crystallization temperatures or even undesired crystalline phases. Three reactions are generally used to describe the sol-gel method:

$$\equiv Si\text{-}OR + H_2O \leftrightarrow \equiv Si\text{-}OH + ROH \quad (1)$$

$$\equiv Si\text{-}OR + HO\text{-}Si\equiv \leftrightarrow \equiv Si\text{-}O\text{-}Si\equiv + ROH \quad (2)$$

$$\equiv Si\text{-}OH + HO\text{-}Si\equiv \leftrightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2O \quad (3)$$

In the hydrolysis reaction the alkoxide groups (OR) are replaced with a hydroxyl group (OH), and condensation commences before the hydrolysis is complete. The condensation reaction, which involves silanol groups, produces siloxane bonds (Si-O-Si) and the by-products alcohol or water [6]. Thin films can be prepared from the precursor solution using spin, dip or spray techniques. We used the dip-coating method for the BSO thin films deposition. When the dip-coating method is used, a substrate is immersed in the precursor solution and withdrawn at a constant rate. During the deposition of the thin film on the substrate the evaporation of the solvent and the condensation occur at the same time. The coating microstructure is determined by the competition between the evaporation of the solvent and the condensation. Compared with other thin-film-forming processes – such as chemical vapour deposition or

sputtering – the sol-gel dip coating requires considerably less equipment, relatively low processing temperatures, and non-vacuum facilities, and is therefore less expensive. However, the most important advantage of sol-gel over other coating methods is the ability to tailor the microstructure of the deposited film by varying the concentration of the sols.

In this paper we report on the synthesis of $Bi_{12}SiO_{20}$ thin films using the sol-gel method from bismuth nitrate and tetraethyl orthosilicate on a sapphire substrate. The aim of this work was to achieve pure $Bi_{12}SiO_{20}$ thin films with a good control over their microstructure. The stability of the solution was also investigated because the chemical stability of the solution directly determines the microstructure of the thin films.

2 EXPERIMENTAL

2.1 Preparation of the Bi-Si solution

The precursor solution was prepared using bismuth nitrate $Bi(NO_3)_3.5H_2O$ and tetraethyl orthosilicate $Si(OC_2H_5)_4$; glacial acid and 2-ethoxyethanol were used as the solvents. First, 98 %-pure bismuth nitrate was dissolved in the glacial acetic acid with stirring at a temperature of 40 °C, for 30 min. This was followed by the addition of tetraethyl orthosilicate under constant stirring for 5 h at room temperature. The precursor solution was diluted with 2-ethoxyethanol to obtain 1.2 M, 1.12 M, 0.98 M, 0.76 M and 0.67 M concentrations.

2.2 Preparation of the thin films

The $Bi_{12}SiO_{20}$ thin films were deposited from the sol using the dip-coating method. The film was deposited at room temperature with a controlled withdrawal speed of 15 cm/min. In the present study, sapphire, quartz and corundum substrates were used for the deposition of the BSO thin films. Prior to use, the substrates were cleaned in an ultrasonic bath followed by drying. The dried gel films were then fired at various temperatures, ranging from 300 °C to 700 °C. Annealing at different temperatures was proceeded with a slow heating rate of 5 °C/min, because a large volume change occurs during heat treatment, which might lead to cracks in the films. The structure of the film was analyzed with an X-ray diffractometer (Bruker, AXS D4) using Cu-K_α radiation. The surface morphology of the thin film was studied using a JEOL 5800 scanning electron microscope (SEM).

3 RESULTS AND DISCUSSION

3.1 Solution characterization

A very important parameter in the sol-gel method is the concentration of the sol, which determines the stability of the sols and the microstructure. It is known that TEOS is immiscible with water; therefore, a mutual solvent 2-ethoxyethanol is used as a homogenizing agent. Dilution of the precursor solution with 2-ethoxyethanol is an important step in the sol-gel procedure, because the 2-ethoxyethanol is not simply a solvent, it can also promote esterification or depolimerization as indicated by the reverse of Eqs. 1, 2 and 3. This leads to restructuring and ultimately results in the formation of highly condense colloidal particles. The effects of sol concentration on the overall hydrolysis and condensation rates was determined by the time required for gelation, and is shown in **Table 1**. The solution with the concentration 0.76 mol/L is stable for 456 h before the gel forms. As the solution concentration increases, the time required for gelation decreases sharply. The solution with concentration 1.2 mol/L is only stable for 5 h before the formation of the gel. The precursor solution with the concentration 0.67 mol/L is not stable because in this case the 2-ethoxyethanol promotes esterification and causes the formation of particles. Any further dilution with 2-ethoxyethanol results in the formation of unstable sols.

Table 1: Effects of sol concentration on the time required for gelation
Tabela 1: Vpliv koncentracije sol-ov na čas gelacije

C / (mol/l)	*t* / h
1.20	5
1.12	48
0.98	168
0.76	456
0.67	–

3.2 Film characterization

Our first goal was to find a suitable substrate for preparing the BSO thin film because the substrate can react with the film as well as having a great influence on the microstructure. We used several substrates for the deposition of BSO thin films: quartz, corundum and sapphire. When we used quartz as a substrate we observed that it reacted with the thin film, and instead of the $Bi_{12}SiO_{20}$ phase, the $Bi_4Si_3O_{12}$ phase forms. The corundum substrate does not have flat surface; therefore, the thin film was distributed unequally on the substrate. In contrast, the sapphire substrate does not react with the thin film and has flat surface. Therefore, we decided to prepare BSO thin films on a sapphire substrate using the sol-gel method. The annealing temperature has a great influence on the phase evolution and microstructure of the thin films. In order to investigate the annealing temperature effect on the phase evolution we analysed X-ray diffraction patterns of the $Bi_{12}SiO_{20}$ thin films deposited on sapphire substrates annealed at 300 °C to 700 °C in air, as shown in **Figure 1**. At a temperature of 300 °C we observed the presence of silicon oxide and bismuth oxide. The thin film heat treated at 300 °C was partly crystalline. When the annealing temperature was increased to 400 °C the film crystallized completely, the peaks of silicon oxide decreased and the bismuth silicate

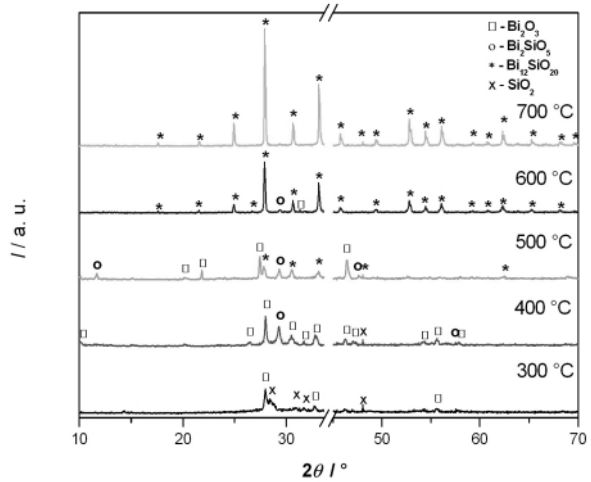

Figure 1: X-ray diffraction patterns of thin films annealed at temperatures from 300 °C to 700 °C (break between 2θ = 33-45° is present to eliminate the sapphire peaks)
Slika 1: Rentgenski difrakcijski spektri tankih plasti, žganih od 300 °C do 700 °C (ustavljeni presledek med 2θ = 33-45° pripada odstranitvi vrhov zaradi podlage)

phase (Bi_2SiO_5) appeared. This indicates a reaction between the silicon oxide and the bismuth oxide. After heating at 500 °C we observed a decrease in the amount of the bismuth silicate phase and the bismuth oxide phase. This observation implies the formation of a new phase, $Bi_{12}SiO_{20}$. At 600 °C almost all peaks belonged to $Bi_{12}SiO_{20}$; however, a small amount of Bi_2SiO_5 and Bi_2O_3 was still present in the film. As the annealing temperature was increased to 700 °C only peaks related to the $Bi_{12}SiO_{20}$ phase were observed. These results suggest that the BSO phase formed at a temperature between 600 °C and 700 °C.

Figures 2 a-c shows the influence of annealing temperature on the microstructure of the thin film prepared from the sol with a concentration of 0.76 mol/L, obtained by scanning electron microscopy. The films were annealed at 300 °C, 500 °C and 700 °C.

A significant variation in the microstructure of the films is observed. As shown in **Figure 2a**, at 300 °C the surface of the substrate is covered with a thin porous layer. If we compare this microstructure with the microstructure of the thin film annealed at 500 °C, which shows great porosity (**Figure 2b**), we can presume that organic compounds are still present in the film annealed at 300 °C. With an increase in the temperature from 300 °C to 500 °C the organic decomposed and a thin porous film formed with an average grain size of 200 nm. In contrast, the film annealed at 700 °C contained much larger grains with a size of around 500 nm. From the porosity, which appears in the microstructure of the film annealed at 300 °C, we can conclude that a large amount of solvent was trapped in the film during gelation. This indicates that the reaction that led to gelation occurs more quickly than the evaporation of the solvent, and the coating becomes a gel before it dries.

Figures 3 a-b presents the surface morphology of the thin films deposited on the sapphire substrate from the sols with a concentration of 0.76 mol/L and 1.12 mol/L

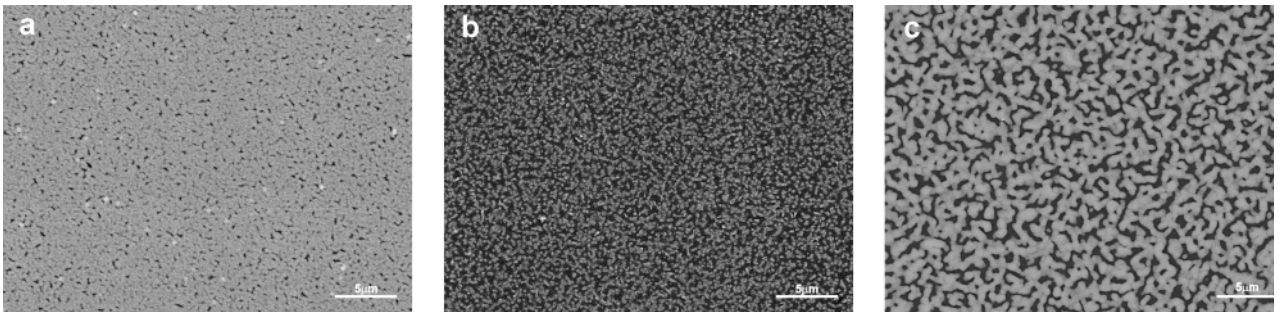

Figure2: SEM micrographs of the microstructure of annealed thin films at a) 300 °C, b) 500 °C, c) 700 °C
Slika 2: Mikrostrukture žganih plasti pri temperaturah a) 300 °C, b) 500 °C, c) 700 °C

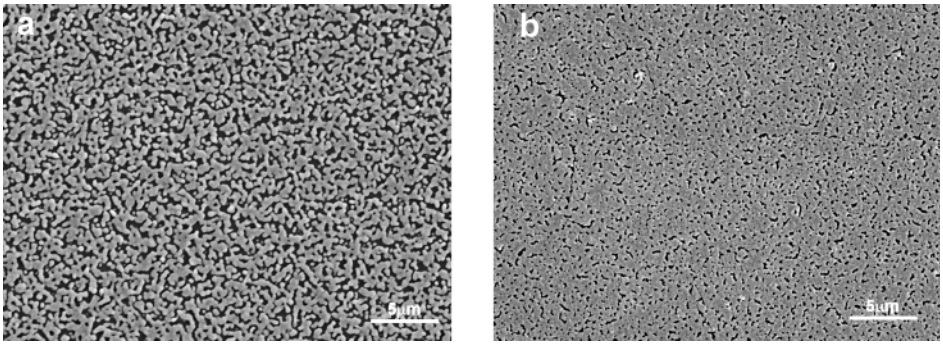

Figure 3: SEM micrographs of the microstructure of thin films annealed at 700 °C deposited from sol a) 0.76 mol/L, b) 1.12 mol/L
Slika 3: Mikrostruktura plasti žganih pri temperaturi 700 °C in nanešenih iz sol-ov a) 0,76 mol/L, b) 1,12 mol/L

obtained using an SEM. For the film dip-coated from the precursor solution with a concentration of 0.76 mol/L (**Figure 3a**) a microstructure with great porosity is observed. The high porosity is a consequence of the large amount of solvent in the sols with a lower concentration. In contrast, the film deposited from the sol with a concentration of 1.12 mol/L (**Figure 3b**) shows a microstructure with less porosity. As the solution concentration increases, so does the viscosity. All the films were deposited under constant conditions, the increased viscosity results in the formation of films with less porosity.

4 CONCLUSION

It can be concluded on the basis of this study that $Bi_{12}SiO_{20}$ thin films can be successfully prepared on a sapphire substrate using a dip-coating procedure and $Bi(NO_3)_3.5H_2O$ and $Si(OC_2H_5)_4$ as the source materials. We observed that with an increasing concentration of the sols the time required for gelation decreased. The composition and microstructure showed a strong dependence on the annealing temperature. The XRD results showed that a single BSO phase was formed in the temperature range between 600 °C and 700 °C. The surface morphology of the films deposited from the 0.76 mol/L and 1.12 mol/L solutions indicates that as the solution concentration increased the grain size decreased, and so a less porous film forms as a result.

5 REFERENCES

[1] M. Jain, A. K. Tripathi, T. C. Goel, P. K. C. Pillai, Journal of Material Science letter, 18 (**1999**) 479–481

[2] M. Valant, D. Suvorov, Chem. Mater., 14 (**2002**), 3471–3476

[3] M. Valant, D. Suvorov, Boletin de la Sociedad Espanola de Ceramica y Vidiro, 43 (**2004**), 634–639

[4] Y. Nagao, Y. Mimura, Japanese Journal of Applied Physics, 24 (**1985**) 2, L954–L955

[5] E. O. Klebanski, A. YU. Kudzin, V. M. Pasal'ski, S. N. Plyaka, L. YA. Sadovskaya, G. KH. Sokolyanski, Physics of the Solid State, 41 (**1999**) 6, 913–915

[6] C. J. Brinker, G. W. Scherer, Sol-gel Science, 1989