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Abstract

The effects of gold-particle incorporation on the structure of barium titanate ($BaTiO_3$) thin films was investigated. $BaTiO_3$ thin films (110 nm thick) with different gold concentrations were prepared via sol-gel processing and analyzed using X-ray diffractometry. The diffraction results showed that the crystal structure of the thin films changed from predominantly the cubic phase to the tetragonal phase, and the crystallite size increased as the gold concentration increased. Possible mechanisms for the gold-enhanced crystallization have been discussed.

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The effects of gold-particle incorporation on the structure of barium titanate ($BaTiO_3$) thin films was investigated. $BaTiO_3$ thin films (110 nm thick) with different gold concentrations were prepared via sol–gel processing and analyzed using X-ray diffractometry. The diffraction results showed that the crystal structure of the thin films changed from predominantly the cubic phase to the tetragonal phase, and the crystallite size increased as the gold concentration increased. Possible mechanisms for the gold-enhanced crystallization have been discussed.

I. Introduction

BARIUM TITANATE ($BaTiO_3$) has been widely studied in several different forms, including powder,[1–3] bulk,[4–6] thin film,[7–12] and multilayer,[13–15] because of its excellent electronic and optical characteristics; these include high dielectric constant, transparency in visible wavelength, and high nonlinear optical susceptibility. To satisfy potential microelectronics applications, thin films of $BaTiO_3$ with good electrical and/or electro-optical properties are required. Several methods are suitable for the formation of thin films. Among these methods, sol–gel,[8–11] chemical vapor deposition,[7] and sputtering[12,13] processes are most widely favored. The sol–gel approach is arguably one of the easiest methods to obtain good-quality films. However, film structure and electrical properties are greatly dependent on annealing and/or deposition temperature, in addition to film thickness and grain size. It has been reported that, after annealing at a temperature of >500°C, the films are crystalline, whereas they remain amorphous at temperatures <500°C.[11]

Noble-metal-dispersed dielectric materials have also been intensively studied,[11,16–19] because the noble-metal particles create an electric field around the particles and, therefore, enhanced electrical and electro-optical properties of these dielectric materials may be expected. Among the noble metals, gold is most intensively studied, because of a special blend of characteristics, including high polarizability, high electronegativity, and a relatively low tendency to react with other pertinent elements.

From this perspective, gold-dispersed $BaTiO_3$ films are expected to exhibit a high dielectric constant and, therefore, be suitable for electronic and microelectronic applications (e.g.,

dynamic random access memories, DRAMS). However, there are few reports in the literature on this material to date.[11]

In this paper, we have used the sol–gel process for the formation of gold-dispersed $BaTiO_3$ films, and the effects of gold addition on the structural properties are investigated via X-ray diffractometry (XRD). Some interesting results of gold-enhanced crystallization and a cubic–tetragonal phase transition are presented and then related to a kinetic model. Finally, some possible mechanisms for the crystallization enhancement are proposed.

II. Experimental Procedure

The sample preparation was conducted in the following manner, as was used by Kineri *et al.*[11] First, 1 mol of $Ba(CH_3COO)_2$ was dissolved in the mixed solution of 20 mol methanol (C_2H_5OH), 25 mol CH_3COOH, and 1 mol glycerol, and then the solution was stirred for 2 h. After stirring, 1 mol of $Ti[O(CH_2)_3CH_3]_4$ was added to the solution, followed by stirring for 2 h. Then, a mixed solution with various specified quantities of $HAuCl_4·xH_2O$[20] and 1 mol of C_2H_5OH was added to the above-mentioned solution. Finally, to form the gold-dispersed $BaTiO_3$ films, the final solution was spin coated onto two different types of *p*-type Si (resistivities, ρ, of 0.5–0.7 and 5–7 Ω·cm) wafers that had been dipped into hydrofluoric acid (HF) prior to spin coating, to remove the native silicon oxide. The conditions for the spin coating were 2000 rpm for 45 s. After the solution was spin coated, all the samples were annealed at 170°C for 1 h in a nitrogen-gas atmosphere, followed by two steps of successive annealing of 400°C for 1 h and 700°C for 1 h in air. The thickness of all the samples prepared using this procedure was ~110 nm, as measured by an α-step profilometer and by using cross-sectional field-emission scanning electron microscopy (SEM).

In this study, the highest annealing temperature (700°C) and thickness of the films (110 nm) were both fixed and only the gold concentration in the solution, and, hence, in the films, was varied. Table I summarizes the sample-preparation conditions. According to X-ray photoelectron spectroscopy (XPS) measurements, the gold concentration for sample 1107B was ~0.5 at.%. Structural evaluation of the films was performed using XRD (D5000 system, Siemens, Cherry Hill, NJ).

Table I.   Summary of Sample-Preparation Conditions

Sample code	$HAuCl_4·xH_2O$ content[†] (mol)	Annealing temperature (°C)	Thickness (nm)
1107A	0	700	110
1107B	0.05	700	110
1107C	0.01	700	110
1107D	0.005	700	110

[†]Per 1 mol of $Ba(CH_3COO)_2$.

III. Results

Figure 1 shows the XRD results for the four different samples. In the sample with no gold (sample 1107A), only a small broad peak is observed, at $2\theta \approx 44.5°$, which can be assigned to the (200) plane of cubic $BaTiO_3$.[2] On the other hand, for the sample with the highest gold concentration in this experiment (sample 1107B), two sharp peaks, at $2\theta = 22.3°$ and $2\theta = 45.5°$, are observed. These two peaks are due to the reflections from the (100) and (200) planes of $BaTiO_3$; the latter peak is, in fact, not from the cubic phase but the tetragonal phase (or perovskite) of $BaTiO_3$.[2,9,21] Also, from the XRD pattern of sample 1107B, it is clear that the film has a larger average grain size and is highly oriented along the [100] direction, despite the use of a (100) Si wafer as a substrate, which has a substantially different crystal structure. The film of sample 1107B shows a small peak, at $2\theta \approx 28.8°$, which has not yet been assigned. By adding a small amount of gold (0.005 mol, sample 1107D) to the $BaTiO_3$ film, the peak intensity for the (200) plane of cubic $BaTiO_3$ increases; however, the peak is still weak and broad. Further additions of gold (0.01 mol, sample 1107C) result in the appearance of an unknown peak at $2\theta = 28.8°$, as is observed in sample 1107B, whereas the cubic (200) peak intensity seems to weaken. From the above-mentioned results, it may be concluded that adding gold to undoped $BaTiO_3$ films enhances crystallization in these films.

IV. Discussion

In this section, we focus on why the presence of gold enhances crystallization in the films. We also examine why gold induces a phase transition from a cubic structure to a tetragonal structure.

Our sol–gel process is very similar to that used by Kineri *et al.*,[11] who examined the effects of heat treatment on the structural and optical properties of $BaTiO_3$ thin films after spin coating, using XRD and infrared spectroscopy. Their results showed that (i) most of the organic matter and water could be removed from the films by annealing at 500°C, (ii) at 500°C, the $BaTiO_3$ films are still amorphous while the gold particles have already crystallized, and (iii) when annealed at 600°C, $BaTiO_3$ films show crystallinity, although the kinetics of structural changes in these films were not stated in their paper. In addition to the above-mentioned results obtained by Kineri *et al.*,[11] our XPS results show that most of the chlorine ions brought into our $BaTiO_3$ films with gold are removed from the films (the detection limit for chlorine via XPS is ~0.1 at.%). Hence, in our case, only the influence of gold particles on the primary crystallization of $BaTiO_3$ films from the amorphous phase should be considered.

Much work has been focused on the tetragonal–cubic phase transition in this material.[22–28] It is widely accepted that oxygen vacancies and internal stress contribute to crystallite growth and phase transformation in $BaTiO_3$ and that $BaTiO_3$ with a large grain size has a tendency to be tetragonal. Although there is little information on the effects of adding gold particles to the structure of $BaTiO_3$, there are several possible explanations why gold particles enhance crystallization; these include substitutional doping,[29] oxidation of metal particles,[30] liquid-phase mediation,[31] internal stress,[32] electric field,[33] and heterogeneous nucleation. We will now examine whether these possible causes are likely to occur in our case.

For the case of substitutional doping, Hsiang *et al.*[29] studied the effects of lanthanum and manganese doping on the structure of $BaTiO_3$ powders. These dopant atoms can be located in substitutional sites and, consequently, create either oxygen or cation vacancies. Their findings were that manganese doping enhances crystallite growth, because of the increase of oxygen vacancies, whereas lanthanum doping causes a decrease in the concentration of oxygen vacancies and, therefore, crystallite growth is inhibited at high temperatures. They also found that doping with lanthanum and manganese increases the internal strain. In addition, it increases the crystallite size, under specific conditions, from 30 nm to 100 nm, because of the presence of cation or oxygen vacancies. However, in the present case, substitutional doping by gold is less likely to occur.

A good example of the effects of oxidation of metal particles has been described by Emoto and Hojo.[30] They studied the effects of nickel particles that were dispersed in $BaTiO_3$ powders on dielectric characteristics. They also observed a decrease in tetragonality with increases in nickel addition. Although they did not mention the reason why the tetragonality decreased by adding nickel particles, their discussions that related to oxidation of the nickel particles in the $BaTiO_3$ matrix implied an increased oxygen vacancy concentration in the structural transformation.

In the case of liquid-phase mediation, specific oxides that melt at relatively low temperatures are added mainly to permit the resulting liquid phase to modify the microstructure. In the case of gold additions to $BaTiO_3$ films, gold particles themselves do not melt at 700°C, and no evidence of any eutectic phases have been detected in this study. Therefore, this possibility is neglected.

The additional internal stress (probably compression due to the addition of gold particles in the film) could be one contributing factor in the enhancement that is observed in our case.
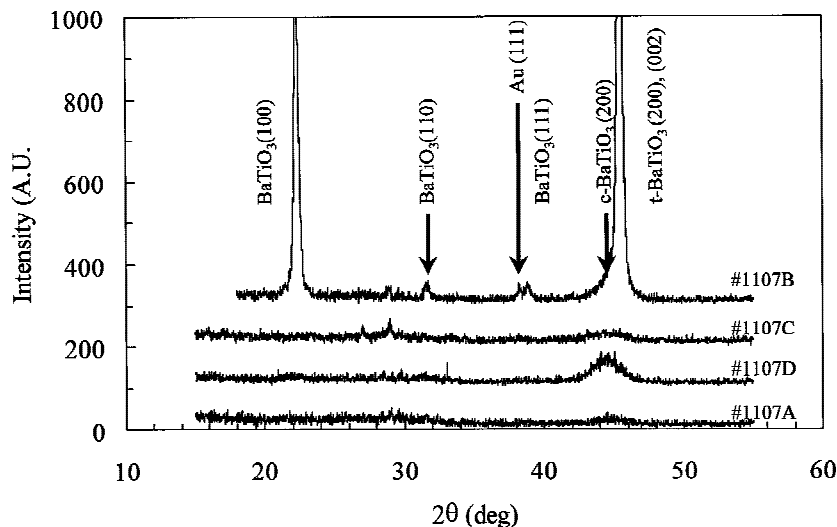

Fig. 1. XRD results for the four samples given in Table I, showing a phase change from cubic to tetragonal and grain growth with increasing gold concentration.

The experimental results observed by Hwang *et al.*[32] are in contradiction to the results by Hsiang *et al.*,[29] in terms of the role of oxygen vacancies. The Hwang *et al.* studies focused on the effects of silicon carbide (SiC) particulates incorporated in the $BaTiO_3$; they observed that, as the SiC content increased, (i) the structure of the $BaTiO_3$ changed from the tetragonal phase to the cubic phase, (ii) the Curie temperature decreased, (iii) the grain size decreased, and (iv) the carrier concentration increased. According to their discussions, these results may be caused by an increase in the oxygen vacancy concentration and residual stress that resulted from the SiC particulate additions. The internal stress is well-known to be able to contribute to atomic migration.

Soejima *et al.*[33] investigated the effects of electric field on the $BaTiO_3$ structure by applying an external electric field to cubic $BaTiO_3$ crystals, and these researchers detected some structural changes via XRD. Although they did not discuss the mechanism for such structural changes, we can consider the effects of internal fields in our case as follows. The incorporation of gold particles creates strong local electric fields around the particles, as mentioned in section I, which may assist in electron transfer from the $BaTiO_3$ matrix to the gold particles. This event, in turn, can contribute to a weakening of the bonds between oxygen atoms and cations in the $BaTiO_3$. At high temperatures during annealing, this phenomenon would facilitate atomic migration, compared to films that have no incorporated gold particles.

Finally, in regard to the possibility of the heterogeneous crystallization of $BaTiO_3$ onto gold particles from the amorphous phase, more information is required to answer whether the gold particles do indeed act as nuclei. However, in general, in the presence of nuclei (or seeds for crystallization), crystallization rates are enhanced, because the potential barrier for nucleation is reduced by a factor of Φ ($0 \leq \Phi \leq 1$; Φ is a ratio of volumes of the heterogeneously and homogeneously formed nuclei).[34]

From the above-mentioned discussion, we propose that the main reasons for gold-enhanced crystallization are the presence of additional internal stresses, the internal electric fields that are induced by gold particles, and/or heterogeneous nucleation and growth. To establish the precise mechanism for gold-enhanced crystallization of $BaTiO_3$ films, further studies are needed.

V. Summary

To obtain information on structural changes resulting from gold-particle additions to barium titanate ($BaTiO_3$) thin films, $BaTiO_3$ thin films 100 nm thick with different gold concentrations were prepared via sol–gel processing and evaluated via X-ray diffractometry. The main results of these studies are as follows:

(1) Additions of gold to the $BaTiO_3$ films enhance crystallization.

(2) The crystal structure of $BaTiO_3$ films with no and small amounts of gold is cubic and has a fine grain structure.

(3) As the gold concentration is increased in the films, the structure has a tendency to become more tetragonal and show a strong texture in the [100] direction.

Possible mechanisms for the enhancement have been discussed. The presence of internal stress, internal electric fields, and/or heterogeneous nucleation and growth are proposed as being the main contributing factors.

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