Transactions of the Materials Research Society of Japan 25 [1] 189-192 (2000)

Low Temperature Fabrication of PZT Thin Films

Kun'ichi Miyazawa and Makoto Kuwabara
Department of Materials Science, School of Engineering, University of Tokyo, Tokyo, 113-8656, Japan
Fax: +81-3-5841-8653, e-mail: miyazawa@ecl.mm.t.u-tokyo.ac.jp

Structure of PZT thin films prepared at low temperatures was examined for the films with and without C_{60}. Addition of a small amount of C_{60} dissolved into toluene enhanced the growth of perovskite crystals with a preferential <001> orientation on $Pt/Ti/SiO_2/Si$ substrates and suppressed the formation of pyrochlore phase, while excessive addition of the toluene solution of C_{60} led to the enrichment of pyrochlore phase. Acetic acid contained in the PZT solution wetted the Pt-coated substrates well. A uniform dispersion of carbon was observed in the C_{60}-doped PZT film prepared at 400°C, indicating the uniform dispersion of C_{60}. An AFM observation of the PZT film prepared at 400°C showed a very smooth surface which reflects the size of nanocrystalline grains in an initial nucleation stage.
Key words: C_{60}, fullerene, low temperature, PZT, sol-gel

1. INTRODUCTION

Lead zirconate titanate ($Pb(Zr,Ti)O_3$, PZT) ferroelectric thin films are widely used in the field of computer memories, micro actuators, sensors and so on. The PZT thin films are often fabricated by the solution deposition technique which requires thermal decomposition of the PZT sol coated on the substrates. Although this technique is very efficient in preparing PZT films, firing temperatures higher than 600°C have been generally used in order to obtain a well-developed perovskite (Pv) structure. Lower firing temperatures are necessary in order to reduce unfavorable thermal influences upon electrodes and devices formed on the same substrate. Hence, it is necessary to establish the method that enables the low-temperature fabrication of PZT thin films.

It has been reported that vacuum annealing of pyrolyzed amorphous PZT gel enhances the formation of Pv and suppresses the stable pyrochlore (Py) phase.[1] On the other hand, C_{60} has been reported to have a very high affinity for oxygen and to form carbon-oxygen adducts at about 200°C.[2] Hence, the addition of C_{60} into PZT films is of great interest to examine its possibility as an additive to develop the Pv crystals, expecting that C_{60} acts as an oxygen scavenger for Py.

The purpose of this paper is to show the structural characteristics of the PZT films with and without C_{60} which were fired at the temperatures of 400 ~ 600°C.

2. EXPERIMENTAL PROCEDURES

Firstly, a 0.4M solution of PZT (Zr : Ti =52 : 48) (solution A) was prepared from isopropyl alcohol, lead acetate trihydrate ($Pb(CH_3COO)\cdot 3H_2O$, LA), titanium tetraisopropoxide ($Ti(iso\text{-}OC_3H_7)_4$), zirconium tetra-n-propoxide($Zr(O\text{-}n\text{-}C_3H_7)_4$),diethanolamine($NH(C_2H_5O)_2$, DEA) and isopropyl alcohol according to our established method[3]. Second, a toluene solution of C_{60} (99.95%, MER Corporation, USA) with a concentration of $2.2gL^{-1}$ was prepared (solution B). Solutions A and B were mixed, adding DEA and acetic acid in an atmosphere of Ar. Table 1 shows the composition of the PZT solutions. The acetic acid was added to improve the wettability of the solution to the $Pt/Ti/SiO_2/Si$ substrates.

Table 1 Composition (in mL) of the PZT solutions added with C_{60}.

mass%C_{60}	0.4M PZT sol.	Conc.C_{60}-toluene sol.	DEA	Acetic acid
PZT-2.5%C_{60}	1	1.5	0.5	1.0
PZT-5.0%C_{60}	1	3.1	0.5	1.5

The PZT-C_{60} solutions thus prepared and a PZT solution without C_{60} were spin-coated on the Pt-coated Si substrates at a revolution speed of 5000 rpm for 20s, and fired in air at 400 ~ 500°C for 10 min at a heating rate of $50°Cmin^{-1}$. The spin-coating and firing processes were repeated for three times. It is known that C_{60} does not decompose in air at temperatures lower than 500°C for this heating rate. [4]

Single-coated PZT films without C_{60} were also prepared on MgO substrates in air at 400 ~ 600°C with a hold time of 0 ~ 30 min, where the spin coating was done at a revolution speed of 7000 rpm for 20 s.

Structure of the PZT films was examined by X-ray diffraction (XRD, MAC MXP-18, 40kV, 200mA), TEM (Hitachi H-800 (200kV), JEM-ARM1250 (1250kV)), AFM (Shimadzu SPM-9500) and SEM (Shimadzu 8705).

3. RESULTS AND DISCUSSION

3.1 Structure of the PZT Films Prepared on MgO Substrates

XRD patterns of the PZT films prepared on MgO substrates by firing at 400°C ~ 500°C are shown in Fig.1. Peaks corresponding to Pv phase are observed in all the films in addition to the peaks of Py phase. Since the hold time is zero and the heating and cooling rates are fast, the XRD patterns show the initial crystallization stages of the films.

The AFM surface profile of Fig.2(a) shows a roughness smaller than 0.45nm, which is reflecting the fine crystallite sizes of the Pv and Py phases in the beginning of crystallization. The surface roughness, however, remarkably increases when a typical heat treatment condition of 600°C is used as shown in Fig.2(b).

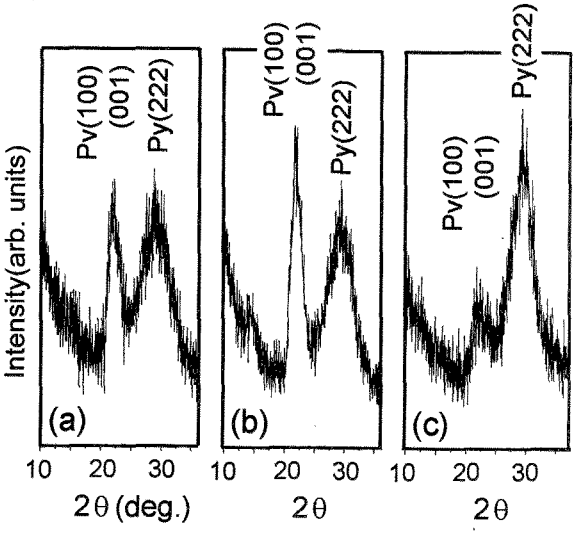

Fig.1 XRD patterns of the PZT films prepared on MgO substrates at (a)400°C, (b)450°C and (c)500°C, respectively, with the heating and cooling rates of 50°Cmin^{-1} and the hold time of 0 min.

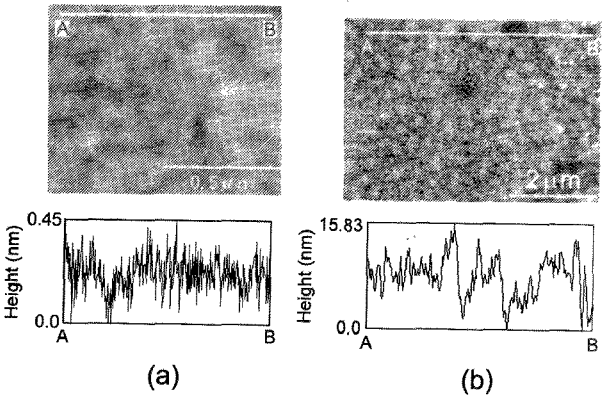

Fig.2 AFM images and surface profiles of the PZT films prepared on MgO substrates at 400°C with the hold time of 0 min (a), and at 600°C with the hold time of 10 min (b), respectively.

Fig.3 shows a Py crystal nucleated in a PZT film prepared on a MgO substrate at 600°C. A large Pv crystal is located in adjacent to the small Py crystal. The Py crystal is found to have nucleated from the amorphous matrix of the specimen. An epitaxial relationship Pv(002) // Py(440) is observed. The size of the Py crystal is a few nanometers, and is comparable to the mean size 1.6nm of the Py crystals which is calculated from the XRD pattern of Fig.1 by using the Scherrer formula. [5]

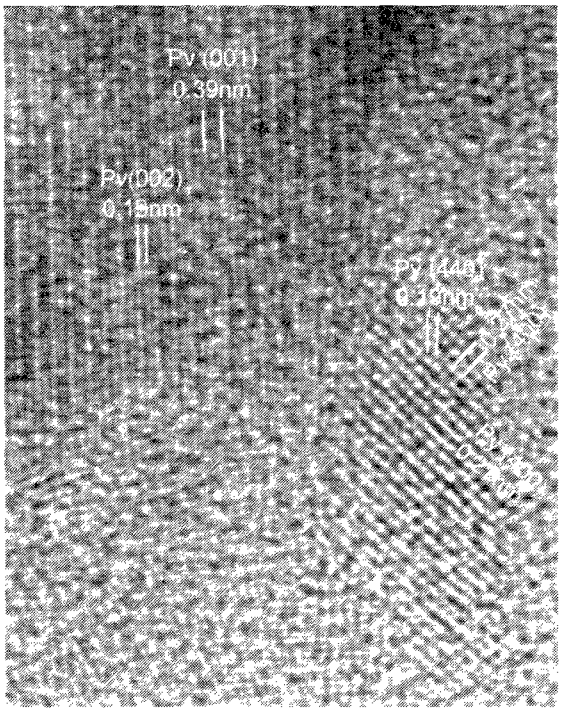

Fig.3 HRTEM image of a PZT film prepared on a MgO substrate at 600°C.

3.2 Structure of the C_{60}-Doped PZT Films

XRD patterns of the PZT films formed on the Pt-coated Si substrates at 400°C are shown in Fig.4, where the film that does not contain C_{60} shows the peaks of abundant Py phase. In the film (Fig.4(b)) doped with C_{60}, however, peaks of Py phase are negligible. Instead, clear Pv peaks with stronger 001 reflections are shown. It is suggested that the addition of C_{60} makes the perovskite formation temperature lower than the reported temperatures of 500°C ~ 600°C.[1,3] This result may be explained by the strong affinity for oxygen atoms of C_{60}. The effect of toluene used as solvent, however, must be also taken into consideration, since toluene may form molecular clusters which behave like C_{60} in water. The effect of acetic acid also must be taken into consideration in the strengthening mechanism of the Pv's 001 reflection. The effect of DEA, however, will be negligible, because a considerable amount of Py phase is

observed in the film of Fig.4(a) which was prepared by use of a solution containing DEA. As is shown in Fig.4(c), addition of too a large quantity of the toluene solution of C_{60} increases the Py phase.

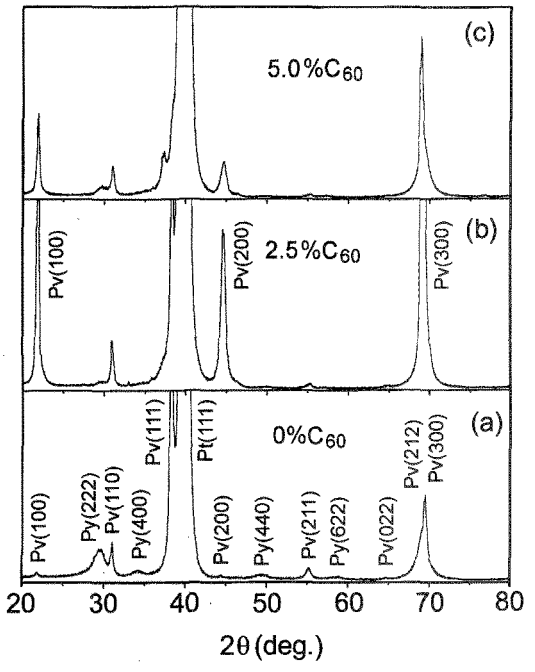

Fig.4 XRD patterns of the PZT films with and without C_{60} prepared on Pt/Ti/SiO_2/Si substrates at 400°C.

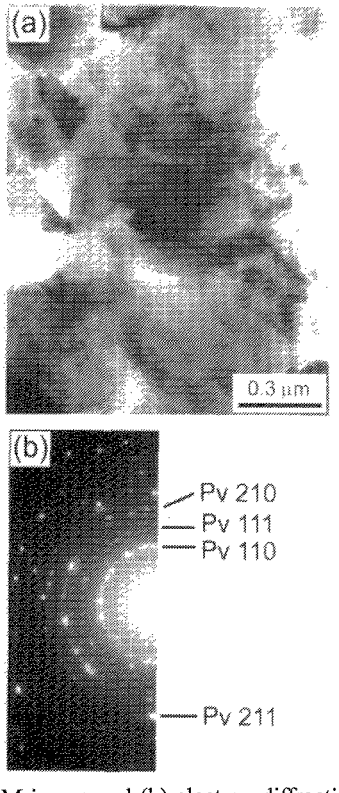

Fig.5 (a)TEM image and (b) electron diffraction pattern of a part of C_{60}-doped PZT film (2.5mass%C_{60}) prepared on a Pt/Ti/SiO_2/Si substrate at 400°C.

It is to be noted that the excessive addition of C_{60} suppresses the growth of Pv crystals.

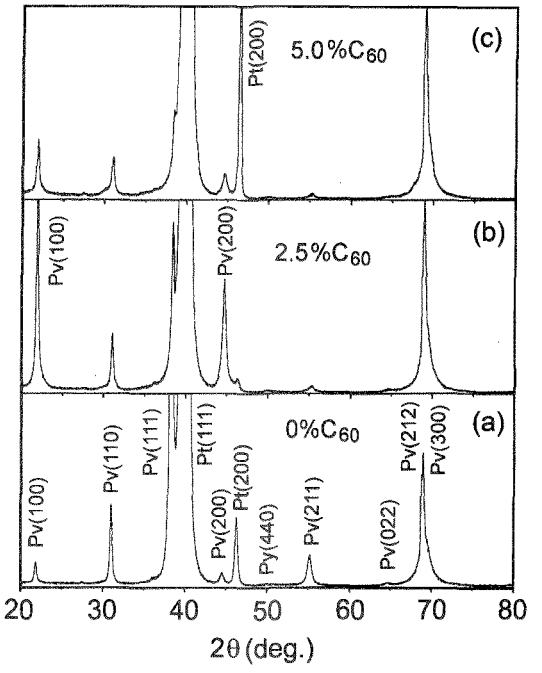

Fig.6 XRD patterns of the PZT films with and without C_{60} prepared on Pt/Ti/SiO_2/Si substrates at 500°C.

The well-developed Pv crystal structure of the C_{60}-doped PZT film is also supported by the TEM observation of Fig.5. In the films fired at 500°C(Fig.6), all the XRD patterns show the formation of Pv phase. It is also found that doping of a small amount of C_{60} (2.5mass%C_{60}) leads to the strengthening of <001> preferential orientation as in the case of Fig.4.

3.3 SEM Observation of the C_{60}-Doped PZT Films

As shown in Fig.7, the C_{60}-doped PZT film has a very smooth surface with no cracks in the observed area. In Fig.8, the constituent elements are found to be uniformly dispersed in the film. Especially, carbon is shown to be uniformly contained. Since it is expected that C_{60} does not decompose in air for the present heat treatment condition, the X-ray image of carbon is considered to show the dispersion of C_{60}, although remaining of a small amount of organic substances other than C_{60} in the PZT film also may not be neglected. The reason for the uniform dispersion of C_{60} is conjectured that the PZT-C_{60} sol was directly spin-coated on the substrate, and the C_{60} molecules were frozen within the coated thin film gel through the rapid evaporation of solvent during the heating process.

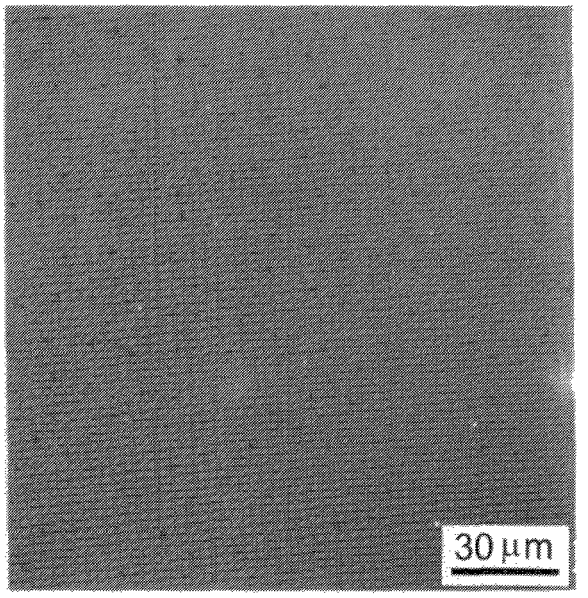

Fig.7 SE image of a C_{60}-doped PZT film (2.5mass%C_{60}) prepared on a Pt/Ti/SiO_2/Si substrate at 400°C.

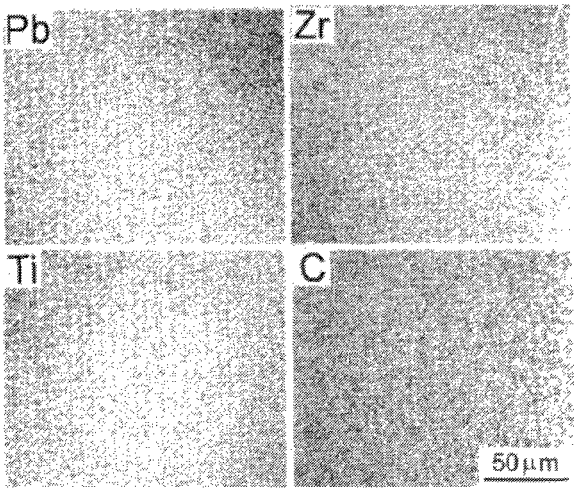

Fig.8 SEM X-ray images of Pb, Zr, Ti and C for the same area as Fig.7.

4. CONCLUSIONS

1. The addition of acetic acid into the PZT-C_{60} sol well wetted the Pt-coated Si substrates.
2. Addition of a small amount of toluene solution of C_{60} into the PZT sol markedly lowered the perovskite formation temperature, suppressing the pyrochlore phase and promoting the <001> preferential orientation of the perovskite PZT films formed on the Pt/Ti/SiO_2/Si substrates.
3. The Py phase was increased by the excessive addition of the toluene solution of C_{60}.
4. A uniform dispersion of carbon was observed by SEM in the film prepared at 400°C, indicating the uniform dispersion of C_{60}.
5. The PZT film prepared at 400°C showed a very smooth surface, while the film prepared at 600°C showed a rougher surface caused by the film crystallization.

ACKNOWLEDGEMENT

The authors are grateful to Dr.Ryutaro Maeda (MEL) for the kind supply of Pt/Ti/SiO_2/Si substrates, and also to Professor Kunio Ito for valuable discussions and suggestions, Mr.Yousuke Ito and Mr.Masashi Kaga (University of Tokyo) for the preparation and characterization of the PZT films, and Mr.Mitsuhiro Nakamura for SEM observations. This study was supported by the Grant-in-Aid for Scientific Research of the Ministry of Education, Science, Sports and Culture, Japan (Subject No.10450247).

REFERENCES

1. V.S.Tiwari, Arun Kumar, V.K.Wadhawan and D.Pandey, Journal of Materials Research, **13**(1998) 2170-2173.
2.H.S.Chen, A.R.Kortan, R.C.Haddon and D.A.Fleming, The Journal of Physical Chemistry, **96**(1992)1016-1018.
3. K.Miyazawa, K.Ito, J.Mayer and M.Rühle, J. Am. Ceram. Soc., **81**(1998)2333-2341.
4. K.Miyazawa, J.Yano, M.Kuwabara, I.Honma and M.Akaishi, J. Am. Ceram. Soc., submitted.
5. B.D.Cullity: Elements of X-ray Diffraction, 2nd ed., Addison-Wesley Publishing Company, Inc., 1978, pp.102.

(Received December 16,1999 ; Accepted January 31,2000)