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Synthesis of pure phase $BiFeO_3$ films grown on Iridium electrode by MOCVD for ferroelectric memories

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1. Introduction

Multiferroic $BiFeO_3$ (BFO) has recently stimulated industries as well as fundamental research because it simultaneously has antiferromagnetic and ferroelectric order at room temperature due to a high Neel temperature (T_N~370˚C) and a Curie temperature (Tc~850˚C), respectively [1-5]. The application of a poly-BFO film to ferroelectric random access memories (FeRAMs) have been attracting much attention because of a lead-free material, much larger remnant polarization (Pr~150μC/cm^2) [6] and a higher Tc compared with the currently employed materials such as poly-PZT (Pb (Zr,Ti)O_3) (Pr~20μC/cm^2, Tc~350˚C) and poly-SBT ($SrBi_2Ta_2O_9$) (Pr~12μC/cm^2, Tc~320˚C). These excellent advantages of the BFO film realize ultra high density FeRAMs beyond 90nm technology [7] and enable FeRAMs to operate in the high temperature circumstances such in a car engine controller. In the state-of-the-art high density FeRAMs, iridium (Ir) bottom electrode is employed due to the compatibility with a CMOS process[8]. Few studies of the BFO growth on the Ir electrode have been reported and its growth method was chemical solution deposition (CSD) [9]. In view of the fabrication of three dimensional ferroelectric capacitors and the growth of the damage-robust high quality films, metalorganic chemical vapor deposition (MOCVD) is much preferable technology [10]. Therefore the feasibility studies of the BFO growth on Ir electrode by MOCVD are strongly required. In this study, the dependences of the BFO film qualities on the growth conditions were investigated in detail and pure phase BFO films were obtained for the first time.

2. Experimental

BFO films were grown by MOCVD on Ir/Ti/SiO_2/Si substrates. The dependences of the BFO crystal structures on an oxygen flow rate, a substrate temperature and a volumetric liquid source supply mixing ratio of Bi/(Bi + Fe) were investigated. The growth conditions are summarized in table1. The schematic diagram of the double-layered deposition method is shown in fig.1. Crystal structures were examined by a typical θ-2θ X-ray diffraction scan (XRD). The Miller indices of a BFO were identified based on the pseudocubic structure. We have evaluated the film structures, surface morphologies and ferroelectric properties by using the scanning electron microscopy (SEM), the atomic force microscopy (AFM), piezoelectric force microscopy (PFM) and polarization-electric field (P-E) hysteresis loop measurements. The ferroelectric capacitors with top Pt electrodes were fabricated by lithographical lift-off process. In PFM observation, the film was first poled by a negative dc bias at -4 volts (V) within 3×3 μm^2 area then poled opposite within 1×1 μm^2 area inside the previous poled area. We have also investigated the leakage current path in the films by using conductive AFM (c-AFM). Lined Ir electrodes were fabricated by reactive ion etching (RIE).

3. Results and Discussion

The XRD patterns of the BFO films are shown in figs.2. The peak intensity of the (001) BFO increases as decreasing the oxygen flow rate down to 50sccm in fig.2(a). This strong correlation indicates that the oxygen flow rate is crucial parameter for growing BFO by MOCVD. The pure phase BFO films were obtained at the substrate temperature from 550˚C to 590˚C in Fig2(b). In view of the compatibility with advanced CMOS technology, the BFO growth below 600˚C has a great advantage over the typical PZT and SBT. It's found that the only few percent shift of Bi/(Bi + Fe) ratio from the optimal value was vital for the growth of the pure phase BFO films as shown in fig.2(c). We have proposed double layered deposition method to realize the stable growth of pure phase BFO films against the variations of the growth conditions, especially regarding Bi/(Bi + Fe). In this method, the 1st layer is deposited at oxygen flow rate of 50sccm. The process variation at the 1st step easily induces the impurity phases such as $Bi_2O_2CO_3$ and Bi_2O_3 because of the low oxygen flow rate and low growth temperature below 600˚C. In fact impurity phase of the $Bi_2O_2CO_3$ was observed under the condition of the 5% excess Bi ratio at the 1st layer as shown in fig.2 (d). At the following second step, only the oxygen flow rate is increased typically up to 150sccm. The condition of the high oxygen flow rate enhances the transformation of the Bi rich impurity phases in the 1st layer into BFO as shown in fig.2 (d). It's worth noting that it's seems the excess Bi facilitates forming (101/110)-oriented BFO in fig.2 (d). Finally the dense pure phase BFO films on Ir electrode by MOCVD were obtained as shown in figs.3 and figs.4. Figure 5 shows the out-of-plain PFM image for the 1st layer. We have observed the sharp contrast of the piezoelectric

response between the positive poled area and negative one. It indicates the complete reversible switching and clear proof of ferroelectricity. The clear P-E hysteresis loop has been also observed for the capacitor with double-layered BFO film although the loop shape implied the some leakage current as shown in fig.6. Large leakage current for the capacitor with the 1st layer has been observed. By contraries, the current measured by direct proving on the 1st layer was completely negligible as shown in fig.7. Figures 8 show the AFM image and c-AFM map on the same region for the 1st layer. We have found that the points with the high current signal correspond to the pinholes. These results indicate that the dominant cause of the high leakage current on the capacitor structures is the electrically short between top and bottom electrode through the pinholes in the film. A BFO grows on the Ir electrode according to Volmer-Weber growth mode so that the pinholes are expectedly formed at the place of the collision with more than three grains. We expect that the probability of the collision with multiple grains is reduced by limiting the nucleation area on Ir electrode as shown in fig9 (a). This model is consistent with the SEM image in figs9 (b-e). Figures 10 show the relationship between the lined Ir width and defect density. It's indicated that the growth of the high quality BFO films has been successfully achieved for the ultra high density FeRAMs with submicron-sized capacitors less than 450nm in width.

4. Conclusion

The dependences of the BFO crystal structures on the growth conditions of MOCVD were investigated in detail. It's been found that both oxygen flow rate and Bi/(Bi + Fe) ratio were the crucial parameters to synthesis the pure phase BFO. To hurdle the stable growth of the pure phase BFO against the process variations, we have proposed double-layered deposition method. Finally we have successfully demonstrated the feasible synthesis of the pure phase BFO films without voids grown on the submicron-sized Ir electrode by MOCVD using double-layered deposition method for the first time.

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References

[1] J.Wang et al., Science 299,1719(2003)
[2] C-H.Yang et al., Nature Mater. 8,485(2009)
[3] J. Seidel et al., Nature Mater. 8,229(2009)
[4] S. Y. Yang et al., Nature Nano. 10, 143(2010)
[5] G. Catalan and J. F. Scott., Adv. Mater. 21, 2463(2009)
[6] K. Y. Yun et al., Jpn. J. Appl. Phys., 43, L647 (2004)
[7] S. Kawashima et al., Embedded Memories for Nano-Scale VLSIs, p.p.320-321, Springer (2009)
[8] Y. Shimojo et al., Symp. VLSI Tech. Dig., 150(2009)
[9] Z. Zhong et al., Jpn.J.Appl. Phys., 47,2230(2008)
[10] O. Hidaka et al., Symp. VLSI Tech. Dig., 15.5(2006)

Table I MOCVD growth condition of BFO films

		Growth condition	Crucial 1st layer condition	Typical 2nd layer condition
Precursor materials	Bi	$Bi(C_6H_5)_3$		
	Fe	$Fe(thd)_3$		
Bi/(Bi+Fe) liquid mixing ratio [%]		-2% ~ +6%	optimal value	
Deposition pressure [Torr]		2		
Gas flow rate [sccm]	Ar	200		
	O_2	0-500	50	150
Substrate temperature [° C]		550-600	590	
Substrate structure		Ir / Ti / SiO_2 / Si		

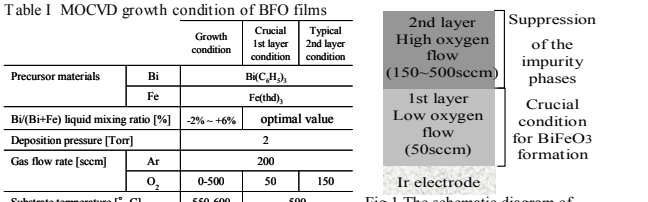

Fig.1 The schematic diagram of the double-layered deposition method

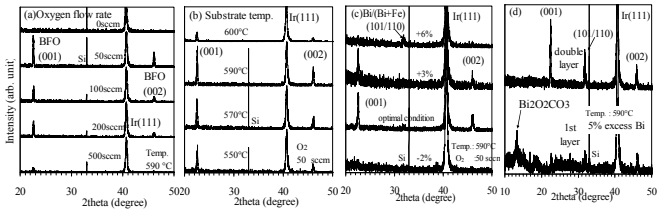

Fig.2 The dependence of XRD patterns on (a) oxygen flow rate, (b) substrate tem-perature, (c) Bi/(Bi + Fe) ratio and (d) film structures.

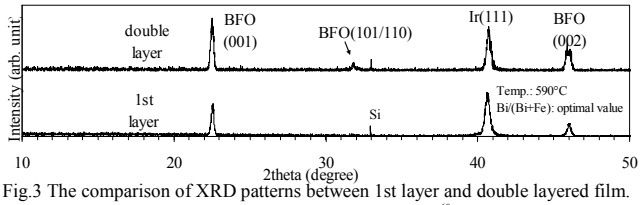

Fig.3 The comparison of XRD patterns between 1st layer and double layered film.

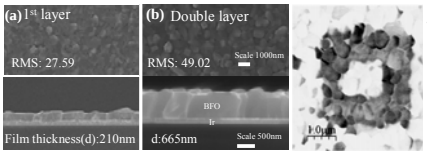

Fig4. SEM images of the surface and cross section of 1st layer and double layered film.

Fig.5 The out-of-plain piezoresponse of the 1st layer by PFM.

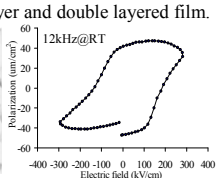

Fig.6 P-E hysteresis loop of the double-layered film.

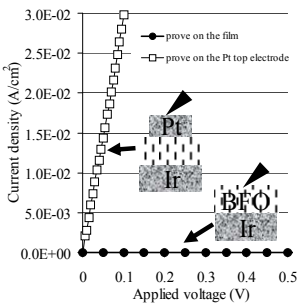

Fig.7 I-V curves by proving on top electrode and film surface.

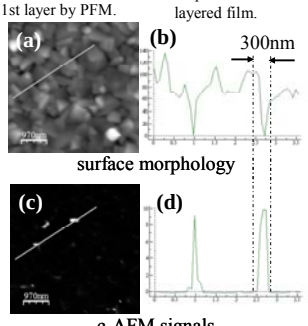

Fig.8 The surface morphology and c-AFM signal of the 1st layer.

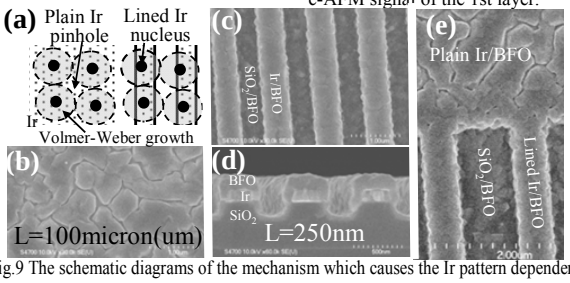

Fig.9 The schematic diagrams of the mechanism which causes the Ir pattern dependence on BFO surface morphologies are shown in (a). SEM images of BFO films grown on (b,e) a plain Ir and (c-e)0.25um lined Ir lined Ir electrodes.

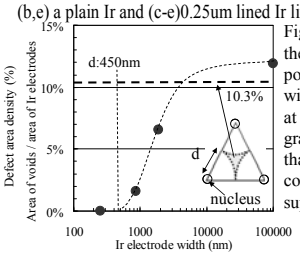

Fig.10 The dependence of the defect density on the Ir width. The estimated distance from the point of the nucleus to the point of the collision with next grains was 450nm based on the data at L=100um in the case of collisions with three grains. It indicated that on the Ir electrode less than 450nm in width, the probability of the collisions are reduced and defects formation are suppressed. It's consistent with the observation.