Characterization of (Ba, Sr)RuO$_3$ films deposited by metal organic chemical vapor deposition

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Received 24 July 2003

Abstract

(Ba, Sr)RuO$_3$ oxide electrodes have been studied for high dielectric (Ba, Sr)TiO$_3$ film in DRAM capacitors. Metal organic chemical vapor deposition (MOCVD) is used for large-scale deposition and provides better step coverage properties. In this work, methoxyethoxytetramethylheptanedionate (METHD) precursor and solvent [n-butylacetate(C$_6$H$_{12}$O$_2$)] were mixed together into a single solution source. Post deposition annealing is carried out in oxygen atmosphere using rapid thermal annealing (RTA) to investigate the effect of organic impurities such as carbon during deposition. After annealing, resistivity of the BSR film decreased drastically compared to the as-deposited film. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis were used to describe this phenomenon accurately. The decrease in carbonate with increasing annealing time was confirmed by XRD analysis.

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1. Introduction

(Ba, Sr)TiO$_3$ [BST] has a high dielectric constant and it has been receiving a great deal of attention for use in next generation ultra-large scale integrated dynamic random access memories (ULSI-DRAMs) [1–3]. Not only BST itself but also the electrode material for the BST film has been extensively studied since the properties of BST films such as the dielectric constant and leakage current density are strongly affected by the bottom electrode [4–6]. In this work, we propose a (Ba, Sr)RuO$_3$ [BSR] oxide electrode which has an outstanding structural match with BST and which is chemically compatible with BST. Furthermore, it was demonstrated that the formation of an interfacial layer could be avoided due to these similarities [7]. BSR films were deposited by metal organic chemical vapor deposition (MOCVD) in this study because the CVD process has excellent advantage in large-scale deposition and good step coverage. In spite of these advantages, a problem associated with the MOCVD process is the degradation of film properties originating from residual impurities such as carbon in the metal-organic source. Many studies have listed this problem to explain the degradation of film properties [8–10].

In this paper, the change of the chemical composition is analyzed by X-ray photoelectron spectroscopy (XPS), which provides valuable information on oxidation states and surface composition [11], and how a residual impurity, such as carbon, leads to the degradation of the BSR film properties was examined. Through the post deposition annealing with various annealing times, we discuss the relationship between phase transformation and resistivity of the BSR film.

2. Experimental

Fig. 1 shows a schematic diagram of the deposition system used for BSR film preparation in this study. A liquid delivery system (LDS) was used for carrying the source and the length of source delivery line was minimized for preventing condensation of the precursors. Fig. 2 presents the molecular structures of the barium precursors such as tetramethylheptanedionate (C$_{11}$H$_{19}$O$_2$: TMHD) and methoxyethoxytetramethylheptanedionate (C$_{18}$H$_{25}$O$_4$: METHD) used in our experiment. Ba(METHD)$_2$ tetraglyme, in which one of the CH$_3$
groups in TMHD ligand is exchanged with the CH₂OCH₂CH₂OCH₃ group that appears to surround the Ba²⁺ ion more effectively than the simple TMHD ligand, has a more bulky structure. The METHD precursors are liquid at room temperature, while the TMHD precursors are in the form of solid phase. Most of the experiments in this study were carried out using METHD base source. Ba(METHD, 0.035 mol/l)₂, Sr(METHD, 0.025 mol/l)₂, Ru(METHD, 0.024 mol/l)₃ precursors were mixed into a single cocktail source with the addition of solvent [n-butylacetate(C₆H₁₂O₂)]. The single cocktail source was introduced into a vaporizer via a liquid mass flow controller (LMFC) using Ar carrier gas through a gas nozzle, and then the vaporized gas was mixed with O₂ in the reactor chamber. The quartz dome was heated to 350 °C using a bell-jar heater for the activation of vaporized source. Substrate temperature was maintained at 550 °C and the heat module was rotated at 4 rpm in order to get better uniformity of BSR films. A block heater was set to 280 °C to get the maximum efficiency in vaporization of the precursors. The gas mixture was then injected onto a heated substrate, and subsequently, BSR thin films were deposited on a 4 in. Si wafer. The deposition conditions for BSR films are summarized in Table 1. Post deposition annealing was performed at 700 °C in oxygen ambient using rapid thermal annealing (RTA) at various annealing times.

X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis were used to identify the crystalline phase and the variations of interatomic binding state of each element.

Table 1: Deposition conditions of BSR films by MOCVD

<table>
<thead>
<tr>
<th>Deposition variables</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition temperature</td>
<td>550 °C</td>
</tr>
<tr>
<td>Vaporization temperature</td>
<td>280 °C</td>
</tr>
<tr>
<td>Belljar temperature</td>
<td>350 °C</td>
</tr>
<tr>
<td>Source flow rate</td>
<td>0.075 sccm</td>
</tr>
<tr>
<td>Flow rate of reactive gas (O₂)</td>
<td>250–400 sccm</td>
</tr>
<tr>
<td>Flow rate of carrier gas (Ar)</td>
<td>200 sccm</td>
</tr>
<tr>
<td>Working pressure</td>
<td>2 Torr</td>
</tr>
<tr>
<td>Rotation rate</td>
<td>4 rpm</td>
</tr>
<tr>
<td>Substrate</td>
<td>4 in. p-type silicon</td>
</tr>
</tbody>
</table>
3. Results and discussion

The formation of the crystalline phase is of great importance in BSR film not only as an electrode with low resistivity but also as a template for the epitaxial growth of BST film on it [7].

Fig. 3(a) and (b) present XRD patterns of BSR films deposited with different oxygen flow rates ranging from 250 to 400 sccm before and after annealing, respectively. As-deposited films show (Ba, Sr)CO$_3$ and Ru phases and there is no indication of the formation of the BSR phase (Fig. 3(a)). However, after annealing at 700 °C using rapid thermal annealing (RTA) system for 5 min in oxygen atmosphere, BSR (110) phase appeared in all the BSR films and the best X-ray result was obtained when the oxygen flow rate was 350 sccm during the deposition.

The thermo-gravimetric/differential scanning calorimetry (TG/DTA) curves of Ba(METHD)$_2$, Sr(METHD)$_2$ and Ru(METHD)$_3$ in flowing argon are shown in Fig. 4. These data reveal that Ba(METHD)$_2$ and Sr(METHD)$_2$ have higher decomposition temperatures than Ru(METHD)$_3$. The reason why there was no BSR phase before the annealing could be associated with the possibility that Ba and Sr precursors were not decomposed completely owing to their higher decomposition temperature relative to Ru precursor which interrupted the reaction between ruthenium and other atoms such as barium and strontium [12].

Since the nature of the metal organic precursors has the greatest influence on deposition, we compared the two most popular precursors for the deposition of BSR films, TMHD base source and METHD base source [12,13]. X-ray results of BSR films deposited by TMHD and METHD base sources are shown in Fig. 5(a) and (b), respectively. In the case of the TMHD base source, preferentially oriented crystalline BSR (110) phase was obtained both from as-deposited and annealed films and

![Fig. 3. XRD patterns of BSR films with different oxygen flow rates (a) before annealing, (b) after annealing at 700 °C.](image)

![Fig. 4. TG/DTA curves of METHD source (a) Ba(METHD), (b) Sr(METHD) and (c) Ru(METHD).](image)
there is no noticeable difference between two films. However, TMHD base sources are typically solid at room temperature and are apt to plug the liquid delivery line due to condensation and this problem results in extremely low reproducibility of BSR films in deposition [13]. On the other hand, METHD base sources do not plug the line and have relatively good reproducibility. However, the vaporized ruthenium atom has less chance to react with the other atoms such as barium and strontium because it is difficult to get complete decomposition of barium and strontium precursors due to its higher decomposition temperature in the METHD source compared to the TMHD source. Such an incomplete decomposition of the METHD metal organic precursors in the reaction chamber is likely to make it harder for the formation of the crystalline phase.

The variation of resistivity with different post annealing times is shown in Fig. 6. As deposited BSR films demonstrate too high a resistivity for use as a bottom electrode in DRAM capacitors. However, the resistivity of BSR film is drastically reduced with a 10 s post annealing. As the annealing time is increased, the resistivity value changes slightly, but it is in the acceptable error range. This significant reduction in the resistivity is due to either crystalline phase formation of BSR or the decomposition of undesired carbonate phases in the films.

In order to understand the relation between the electrical resistivity and annealing time, XRD patterns of BSR films at the different post annealing times were compared Fig. 7. The major phases of as-deposited BSR films are initially (Ba, Sr)CO$_3$ and Ru phases. The intensities of these peaks decrease gradually as the annealing time increases, while that of the BSR (110) peak gets relatively stronger. In addition, Fig. 6 reveals that a significant reduction of the carbonate phase can
occur in only 10 s, and the completion of the phase transformation can be accomplished in 5 min.

Gradual transformation of the phases during post annealing was studied further by XPS analysis. The XPS spectra corresponding to the as-deposited BSR and annealed BSR at different times are shown in Fig. 8. One major concern regarding the interpretation of BSR system with XPS analysis is the peak overlap of C 1s and Ru 3d_{3/2}. In order to separate these peaks numerically, the ratio of orbital splitting in Ru 3d_{5/2} and 3d_{3/2} was assumed to be 3:2 [14,15] and the carbon 1s peak was set at 285 eV. XPS spectra of the as-deposited BSR film shows in Fig. 8(a). The peak position of the ruthenium at 280.4 eV implies that most of the ruthenium remains as pure metallic phase with a minor portion of ruthenium in an oxidation state of Ru^{4+} (peak at 282 eV). The unexpected peak at 290 eV is thought to originate from the bonding between carbon and oxygen [16,17]. This bonding leads to the formation of an undesirable carbonate phase which causes the resistivity of the film to increase. In Fig. 8(b), the carbonate peak is noticeably decreased compared to Fig. 8(a). The pure metallic ruthenium peak which is at 280.4 eV, almost disappeared, where as the oxidized ruthenium (Ru^{4+}) peak is mostly dominant in Fig. 8(b). Therefore, as the annealing time increases, not only does this carbonate peak decrease, but the ruthenium in the BSR film becomes more and more oxidized as well. The decomposition of the carbonate compound and the formation of BSR phase are presumably through the follow reaction:

\[(\text{Ba, Sr})\text{CO}_3(s) + \text{Ru}(s) + \text{O}_2(g) \rightarrow (\text{Ba, Sr})\text{RuO}_3(s) + \text{CO}_x(g)\].

From the viewpoint of resistivity variation in BSR films as we have discussed earlier, one can consider that both the decomposition of the highly resistive carbonate phase and the formation of BSR phase play an important role.

4. Conclusion

BSR films were deposited by metal organic chemical vapor deposition using two different kinds of single cocktail sources. TMHD base source turned out to be a good precursor because one can obtain good crystalline phase of BSR films even before annealing unless there is a problem of line-plugging in liquid delivery system, which leads to an extremely low reproducibility in deposition. Such a line-plugging problem did not happen in METHD source which is a liquid form at room temperature. However, as-deposited BSR film consists of (Ba, Sr)CO_3 and Ru phases instead of the BSR phase. Therefore, it requires an extra annealing process. After rapid thermal annealing in oxygen ambient, this carbonate phase was removed and the conductivity of BSR film increased. The results of XPS analysis of the BSR films annealed at different times indicates that the as-deposited BSR thin film contains mostly (Ba, Sr)CO_3 (carbonate) and pure metallic Ru phases. Through the post annealing process, it was confirmed that both the intensity of C with O (carbonate) peak from the (Ba, Sr)CO_3 and pure Ru3d doublet peak decrease gradually and the Ru^{4+} (oxidized Ru) peak increases.
Consequently, the cause of the improvement in resistivity during rapid thermal annealing is believed to be related to the decomposition of the C with O (carbonate) in (Ba, Sr)CO₃ and the increase in the amount of more conductive BSR phase.

Acknowledgements

This work was financially supported by LG Yonam Foundation.

References