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Influence of doped Ag^+ on multifunction characteristics in $SrTiO_3$ ceramics ①

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Abstract: $SrTiO_3$ capacitor-varistor multifunction ceramics is fabricated by a single-sintering process. The research is carried out, mainly aimed at the influence of the doped Ag^+ on multifunction characteristics in $SrTiO_3$ ceramics and its mechanism. The results show that the density of grain-boundary acceptor state increases effectively due to the fact that Sr^{2+} on grain surface is substituted by doped Ag distributing at grain-boundary in form of Ag^+ during the course of oxidizing annealing, which is proposed to be the fundamental reason for understanding the significant difference of both the dielectric properties and varistor properties in $SrTiO_3$ ceramics samples with various Ag^+ contents.

Key words: $SrTiO_3$ ceramics; capacitor-varistor multifunction; Ag^+ doping **Document code:** A

1 INTRODUCTION

$SrTiO_3$-based multifunction ceramics is a kind of new semiconductor ceramics with the dual functions of ceramics grain-boundary-layer (GBL) capacitor of high capacitance and varistor, which exhibits considerable value of further research and remarkable potential of being widely applied in electronic circuits for absorbing wide frequency noise, fast rising up pulse noise and electrical surge. Since $SrTiO_3$ multifunction ceramics was firstly developed by Yamaoka *et al* in 1983 with a two-step sintering process[1], i. e., sintering the ceramics in a reductive atmosphere for the semiconducting of grain and then painting a paste containing diffused ions on the surfaces of sintered ceramics followed by an oxidizing annealing for the diffusion of painted ions, most succedent researchers adopt the process[2~5]. For it is requisite for the painted ions to fully wet the surfaces of the semiconducting ceramics[2], the painted acceptor ions successfully used in the two-step sintering process are finitely monovalent alkali metal ions such as Li^+, Na^+ and K^+ [2,3]. The recent research report on fabricating $SrTiO_3$ multifunction ceramics by a single-sintering process[6] has drawn much attention not only because of its simplicity but also the much more possibilities of selecting acceptor dopant ions, which provides new approaches for promoting the investigation, development and application of the material. In this work, $SrTiO_3$ multifunction ceramics with Ag_2O doped is fabricated by the single-sintering process and investigations are performed with the emphasis on the influence of doped Ag^+ on multifunction characteristics as well as its mechanism.

2 EXPERIMENTAL

$SrTiO_3$ is synthesized by calcining the mixture of $SrCO_3$ and TiO_2 of analytical grade purity. 0.5% (mole fraction) Nb_2O_5 and x% Ag_2O (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5) were used as the donor dopant and acceptor dopant respectively, while a designed amount of SiO_2, TiO_2 and Al_2O_3 were introduced as sintering additives. The components mentioned above were weighted respectively and milled. The milled powder was granulated with PVA solution and pressed into tablets of d 13 mm × (1~ 2) mm. After being burned out organic binder at 600 ℃, the tablets were sintered at 1 450 ℃ for 4 h in a reductive atmosphere(N_2∶H_2 = 4∶1) and then furnace-cooled to 1 150 ℃ for 1 h oxidizing annealing. The sintering process was performed in a sealed corundum tube furnace in which the flow of gas and alteration of atmosphere were available.

The sintered $SrTiO_3$ ceramics samples were polished on both surfaces into 1mm thickness and Ag-Zn electrodes are fired to provide ohmic contact for electrical measurement. The varistor properties and dielectric properties were measured by an MY automatic varistor meter and an HP4275A multi-frequency LCR meter, respectively. The measurement of the AC complex impedance spectroscopy was performed in frequency range of 5 Hz ~ 13 MHz with an HP4192A LF impedance analyzer controlled by a computer. The XPS investigation was carried out using an ESCALAB MK multi-technique electron spectrometer. The XRD analysis was performed at an HZG4-PC X-Ray diffraction meter.

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3 RESULTS AND DISCUSSION

3.1 Influence of Ag_2O content on the multifunction characteristics in $SrTiO_3$ ceramics

The varistor properties and dielectric properties for $SrTiO_3$ ceramics samples with different Ag_2O content are shown in Fig. 1(a) and (b) respectively. It can be seen that the nonlinear coefficient, α, and varistor voltage, V_{1mA}, tend to rise with the increase of Ag_2O content, $x(Ag_2O)$, whereas the apparent permittivity, ε_{eff}, and dissipation factor, tg δ, decrease. The result indicates that the doping of Ag_2O has a significant effect on both the varistor properties and dielectric properties.

3.2 Analysis of the AC impedance spectroscopy

The AC impedance spectroscopy plots using the data measured at room temperature for $SrTiO_3$ ceramics samples with different Ag_2O content are shown in Fig. 2(a). Since the magnitude of the apparent resistance for measured samples is at 10^7 Ω, which exceeds the measurable range of the impedance analyzer (~ 1.2×10^6 Ω), complete impedance spectroscopy semicircles are not observed. The measured AC impedance spectroscopy plots in the measuring frequency range of 5 Hz~ 13 MHz display as several arcs attributed to the corresponding semicircles, and the curvature radii of these arcs enlarge with the increasing Ag_2O content. Fig. 2(b) shows the impedance spectroscopy plot for the sample of $x(Ag_2O) = 0$ in the high frequency range above 5×10^5 Hz, which reflects more details about characteristics of impedance spectroscopy in high frequency. From Fig. 2(b), it can be clearly found that the high frequency terminal approaches the zero point rather nearly, which suggests a very small resistance or a fully semiconducting condition for $SrTiO_3$ grain. Based on the above characteristics of measured impedance spectroscopy plots, a locus imitation is carried out according to Cole-Cole semicircle in the computer controlling the impedance

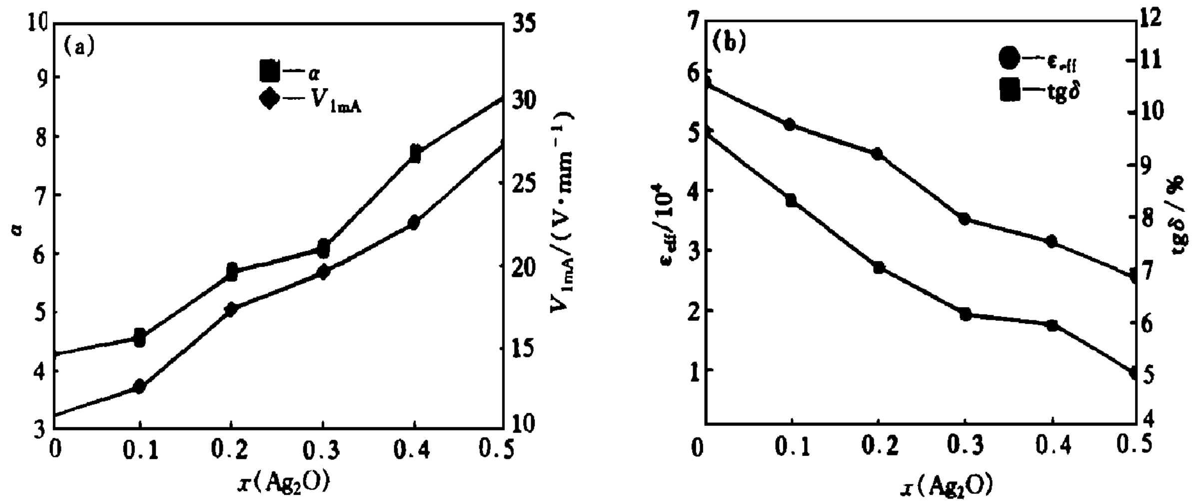

Fig. 1 Relation between multifunction characteristics in $SrTiO_3$ ceramics and Ag_2O content
(a) —Varistor properties; (b) —Dielectrics properties

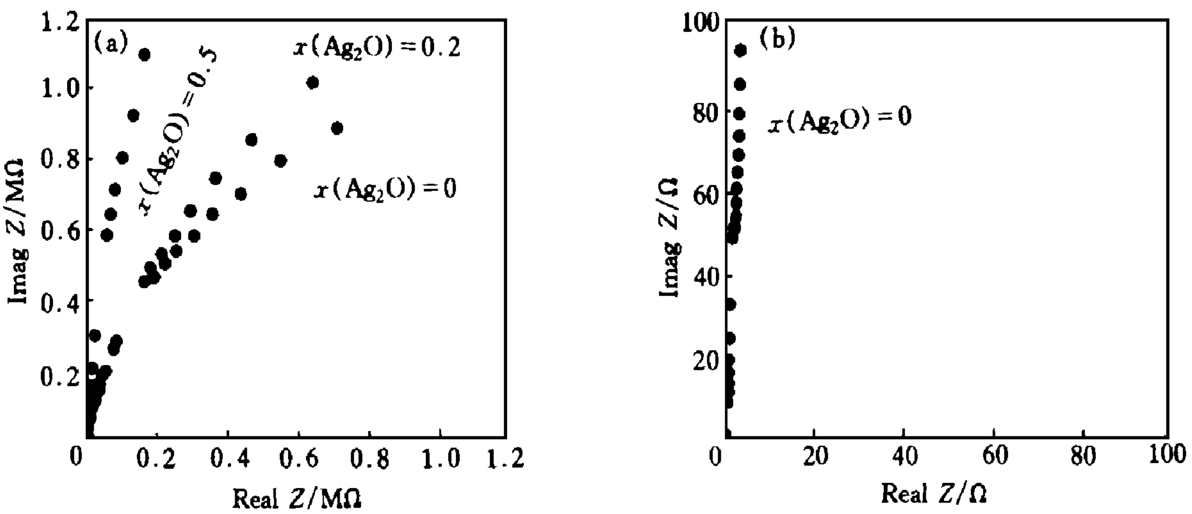

Fig. 2 AC complex impedance spectroscopy plots for $SrTiO_3$ ceramics samples with different Ag_2O content

analyzer. The resistance of grain (R_g) and grain-boundary (R_{gb}) are obtained respectively from the intersects of high frequency terminal and low frequency terminal of the imitated semicircle with Real Z axis[7,8]. The results are shown in Table 1. By comparing the data in Table 1, it is manifested that the resistance of grain for the samples are almost unchanged with the increasing Ag_2O content, while the resistance of grain-boundary for the samples increase continuously. The result refers that the doping of Ag_2O promotes the insulating property of grain-boundary, but generates no evident effect on the semiconducting condition of grain. In light of the measurement results of multifunction characteristics, it can be proposed that the changes of multifunction characteristics as shown in Fig. 1 are associated with the different influences of doped Ag_2O on electrical characteristics of grain and grain-boundary.

Table 1 Effect of Ag_2O content on resistance of grain (R_g) and grain-boundary (R_{gb})

Ag_2O content / %	R_g/ Ω	R_{gb}/ MΩ
0	0.367	4.20
0.1	0.515	4.55
0.2	0.364	5.23
0.3	0.417	5.79
0.4	0.532	6.98
0.5	0.404	9.02

3.3 Structure condition of Ag

Because of the low content in the material and resultant weak photoelectron signals, XPS spectrum of Ag is obtained with the aid of an accumulated counting technique to make the stochastic noise signals offset each other and correspondingly enhance the ratio of photoelectron signal to noise signal. XPS spectrum of Ag 3d electron for the sample of $x(Ag_2O = 0.5$ is shown in Fig. 3. Due to the splitting of energy level of 3d orbit, two photoelectron peaks can be observed, which are attributed to Ag $3d_{5/2}$ and Ag $3d_{3/2}$ with the binding energy of 367.20 eV and 373.20 eV respectively. Moreover, no shaking up lines are detected near the photoelectron peaks. By comparing the XPS characteristics of Ag 3d with that of standard specimen, it can be ascertained that Ag exists in form of Ag^+.

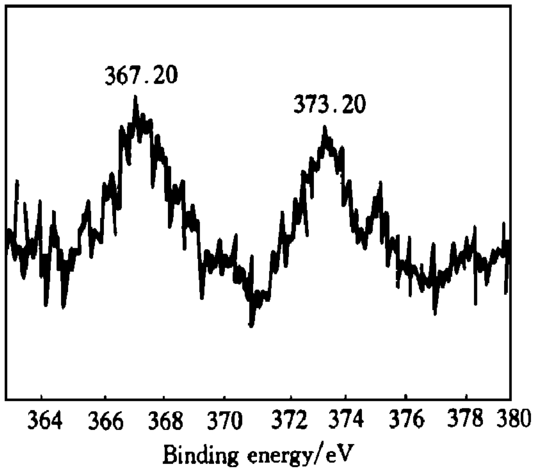

Fig. 3 XPS spectrum of Ag 3d after accumulated counting for 10 times

The XRD patterns of $SrTiO_3$ ceramics samples with different Ag_2O content are shown in Fig. 4. The single phase structure of perovskite (ABO_3) is identified in samples either with or free of Ag_2O doped. Examining XRD patterns of the samples with varied Ag_2O content precisely, it should also be noted that the values of d for corresponding diffraction peaks are entirely the same and no distinct difference is discovered among the intensities for the corresponding diffraction peaks. With the completely same sintering conditions and the sole compositional difference in variation of Ag_2O content, the result implies that the doping of Ag_2O does not induce the change of lattice constants for perovskite structure. Therefore, it can be deduced that the doped Ag^+ does not incorporate into $SrTiO_3$ lattice, which is confirmed by an EPMA investigation[9].

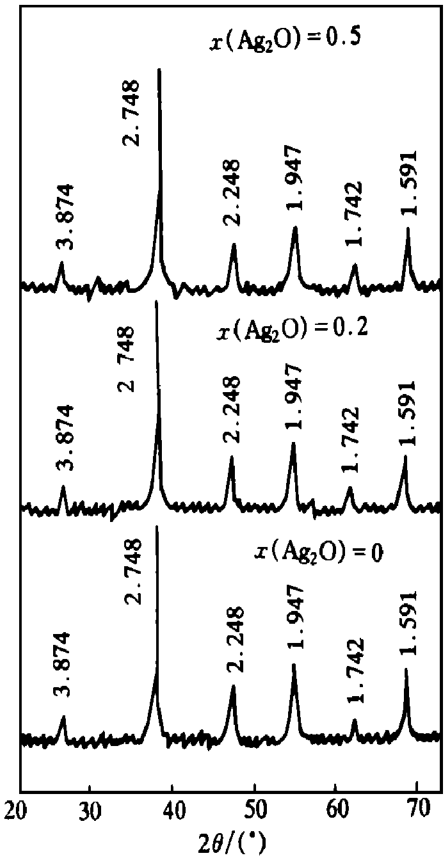

Fig. 4 XRD patterns of $SrTiO_3$ ceramics with different Ag_2O content

Owing to the ionic radius matching between Ag^+ and Sr^{2+} with ionic radius of 126 pm and 113 pm respectively (the relative difference is less than 15%), Ag^+ may substitute Sr^{2+} on A site in $SrTiO_3$ lattice as acceptor dopant according to the following defect reaction:

$$Ag_2O \xrightarrow{SrO} 2Ag'_{Sr} + O_O^{\times} + V_O^{\cdot\cdot}$$

However, it must be mentioned that the occurrence of the defect reaction is controlled by the concentration of oxygen vacancy in $SrTiO_3$ lattice. In fact, the volatilization of lattice oxygen is dominant with the coexistence of donor dopant and low oxygen partial pressure during the course of reduction sintering at high temperature[10]. The resulting oxygen vacancy of high concentration restrains the solution of Ag^+ in $SrTiO_3$ lattice as the defect reaction describes. In the case of presence of the active liquid formed by sintering additives of SiO_2, TiO_2 and Al_2O_3 at high temperature, Ag^+ is thought to dissolve in the active liquid and segregate at grain-boundary[2,5]. During the course of oxidizing annealing, the concentration of oxygen vacancy on grain surface decreases because of the diffusion of ambient oxygen into the ceramics and subsequent occupation of oxygen vacancy on grain surface[11]. Accompanying this occurrence, Ag^+ segregating at grain-boundary diffuses in grain surface and serves as effective grain-boundary acceptor with the behavior of substituting Sr^{2+} there. Therefore, it is considered that the increase of Ag_2O content means the enhancement of the density of the grain-boundary acceptor state and brings about great influences on multifunction characteristics of $SrTiO_3$ ceramics as a result. One of these influences is the rise of grain-boundary barrier height, which improves the voltage-current nonlinear effect. The other is the thickening of the depth of grain boundary insulating layer, which relevantly increases the varistor voltage V_{1mA} and decreases the apparent permittivity ε_{eff} and dissipation factor tg δ.

4 CONCLUSIONS

1) The doped Ag distributes at grain-boundary of $SrTiO_3$ ceramics in form of Ag^+.

2) Ag^+ substitutes Sr^{2+} in grain surface during the course of oxidizing annealing, which effectively enhances the density of grain-boundary acceptor state.

3) The nonlinear coefficient α and varistor voltage V_{1mA} increase with the increase of Ag^+ content, where the apparent permittivity ε_{eff} and dissipation factor tg δ decrease.

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