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Enhancement of thermoelectric power factor in $\text{Na}_x\text{CoO}_2/\text{Au}$ multilayers

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$\text{Na}_x\text{CoO}_2/\text{Au}$ thin film multilayers, with the thickness of Au layer of 0.5-12 nm, have been fabricated on *c*- Al_2O_3 by post annealing of the CoO/Au thin film multilayers in Na vapor at high temperature in air. X-ray diffraction measurements revealed that the resulting Na_xCoO_2 layer was *c*-axis oriented with perfect *ab*-plane alignment and there was no reaction between Au and Na_xCoO_2 . The resistivity of the $\text{Na}_x\text{CoO}_2/\text{Au}$ multilayers decreased significantly with increasing the volume fraction of Au layer without obvious deterioration of the Seebeck coefficient. Consequently, a considerable enhancement of power factor was achieved in $\text{Na}_x\text{CoO}_2/\text{Au}$ multilayers with the right Au volume fraction, which was about 2.2 times larger than that of the single Na_xCoO_2 layer with the same thickness.

Keywords: multilayers; oxides; epitaxial growth; thermoelectric power factor

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1. Introduction

Thermoelectric materials, which can convert heat into electricity and vice versa, are of great interest for application in power generation and solid state cooling [1-3]. The conventional thermoelectric materials are mainly intermetallic compounds and alloys. However, due to surface oxidation and sublimation at high temperature and containing toxic or scarce elements, the practical application of these materials is limited. Oxides can overcome these problems and therefore have attracted increasing attentions to the TE community, particularly to those who are interested in high-temperature applications [4-13]. Recently, layered cobaltites, such as Na_xCoO_2 , $\text{Ca}_3\text{Co}_4\text{O}_9$, $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ and etc., have been widely investigated as promising high-temperature thermoelectric materials due to their good thermoelectric performance [9-13].

The performance of thermoelectric materials is evaluated by the dimensionless figure of merit $ZT=(S^2/\rho\kappa)T$, where S , ρ and κ are the Seebeck coefficient, electrical resistivity and thermal conductivity, respectively. Significant effort to enhance ZT has been devoted in reducing thermal conductivity by making nanostructures and low-dimensional materials [14-18]. Other than the reduction in the thermal conductivity, increasing the power factor, S^2/ρ , is also a critical issue [19]. Recently, several research works demonstrated that the power factor of layered cobaltites can be enhanced by dispersing metal particles into the layered cobaltites matrix [20-23]. Moreover, D. Bergaman and L. Fel have shown that in theory that the power factor of a thermoelectric material can be significantly improved by a multilayered structure

composed of the thermoelectric material and the benign metal, with the right volume fraction of these two components [24]. In this paper, $\text{Na}_x\text{CoO}_2/\text{Au}$ thin film multilayers have been fabricated by a two step method and their high temperature electrical transport properties have been investigated. The results revealed that a significant enhancement of thermoelectric power factor can be achieved in the multilayers, being about 2.2 times higher than that of the pure Na_xCoO_2 single layer with the same thickness at the highest measured temperature of 800 K.

2. Experimental

The $\text{Na}_x\text{CoO}_2/\text{Au}$ multilayers (thickness $\sim 140\text{-}180$ nm), composed of 4 layers of Na_xCoO_2 thin film and 3 layers of Au thin film, were fabricated using a two-step process. First, CoO thin films and Au thin films were alternately grown on $c\text{-Al}_2\text{O}_3$ substrate by laser ablation of a Co_3O_4 ceramic target and Au metal target at the substrate temperature of 700°C under the oxygen pressure about 1×10^{-4} Pa. A 308 nm excimer pulsed laser was used for the CoO and Au films deposition, with the laser energy density of 1.5 and 2.0 J/cm^2 , respectively. Then, the CoO/Au multilayers, covered with NaHCO_3 pellets, was sealed in an alumina crucible and postannealed at 750°C for 120 min in air to form the $\text{Na}_x\text{CoO}_2/\text{Au}$ multilayers. In the post-annealing process, the CoO film was first oxidized into Co_3O_4 film at lower temperature of about $300\text{-}500^\circ\text{C}$ and then converted into Na_xCoO_2 film via lateral diffusion of Na vapor into Co_3O_4 film at higher temperature. The Au volume fraction in the multilayers was controlled by changing the thickness of Au layer. Six $\text{Na}_x\text{CoO}_2/\text{Au}$ multilayered samples were made, with the corresponding Au layer thickness was

about 0, 0.5, 2, 4, 8 and 12 nm, respectively. The volume ratio between Au and Na_xCoO_2 in the above six samples was calculated to be about 0, 1.1, 4.4, 8.6, 17.1 and 25.7 vol.%, respectively.

The crystal structure of the multilayers was measured using a Philips X'Pert 4-circle diffractometer with $\text{CuK}\alpha$ radiation. The surface morphology was examined by both scanning electron microscopy (SEM) and atomic force microscopy (AFM). A VG ESCALAB5 x-ray photoelectron spectroscopy (XPS) with Mg $\text{K}\alpha$ ~ 1253.6 eV exciting radiation was used to detect the Au chemical band in the multilayered films. The working pressure in the XPS chamber was approximately 2×10^{-7} Pa. Before the measurement, the sample was etched for about 10 min by low energy Ar^+ in the XPS chamber in order to remove the impurities on the film surface. The electrical resistivity and Seebeck coefficient were simultaneously measured in air by the standard dc four-probe technique in a LSR-3 measurement system (Linseis, Germany) with the heating rate of 5 K/min. Although the above electrical transport measurements were done in a conventional way which was used in many literatures, there is possibility this may not reflect the real performance of such structure when used in a device.

3. Results and discussion

Figure 1a presents x-ray diffraction (XRD) θ - 2θ patterns of $\text{Na}_x\text{CoO}_2/\text{Au}$ multilayers on $c\text{-Al}_2\text{O}_3$ with different Au volume fractions. It can be clearly seen that the relative intensity of Au peaks increases with increasing the volume fraction of Au in $\text{Na}_x\text{CoO}_2/\text{Au}$ multilayers. Apart from $c\text{-Al}_2\text{O}_3$ and Au peaks, all peaks in each

pattern can be indexed to the 00ℓ diffractions from γ - Na_xCoO_2 phase, indicating that the Na_xCoO_2 layer in the multilayers is phase-pure and c -axis oriented. There is no detectable shift of the Na_xCoO_2 (00ℓ) diffraction peak angles for different samples, indicating that Au does not enter into the crystal lattice of Na_xCoO_2 . The calculated c -axis lattice constant of the Na_xCoO_2 layer is about 10.97 ± 0.003 Å, revealing that the Na concentration x is about 0.68 [25]. Fig. 1c is the Au 4f photoelectron core levels obtained from the $\text{Na}_x\text{CoO}_2/\text{Au}$ multilayers with Au of about 17.1 Vol.%. The peaks of Au $4f_{5/2}$ and Au $4f_{7/2}$ are located at 87.6 and 84.0 eV, respectively, which are corresponding to the normal XPS spectra of Au metal [26]. This result further demonstrates that Au does not enter into the crystal lattice of Na_xCoO_2 or alloy with Na but existed as a metallic phase in Na_xCoO_2 matrix.

We also measured the ab -plane alignment information of the Na_xCoO_2 layer for different samples. The Na_xCoO_2 still exhibits epitaxial growth on c - Al_2O_3 even there has a thin Au layer between each two adjacent Na_xCoO_2 layers. Fig. 1b shows ϕ scan of the Na_xCoO_2 (103) peak for the $\text{Na}_x\text{CoO}_2/\text{Au}$ multilayers with Au of about 17.1 Vol.%, where $\phi=0$ is parallel to the [100] direction of c - Al_2O_3 substrate. A sixfold symmetry characteristic of a (00ℓ)-oriented Na_xCoO_2 layer with ab -plane epitaxy is observed, which reveals a “hexagon-on-hexagon” epitaxial growth of the Na_xCoO_2 layer on the c - Al_2O_3 substrate.

All $\text{Na}_x\text{CoO}_2/\text{Au}$ multilayer samples exhibit very smooth surface, with the root-mean-square (rms) roughness being below 2.0 nm when measured by AFM over a 5×5 μm area. It seems that the parallel inserting of a thin Au layer between two

adjacent Na_xCoO_2 layers does not deteriorate the surface quality of the top NaCoO_x layer. Fig. 2a-b display the AFM and SEM surface images of the pure Na_xCoO_2 film without inserting any thin Au layer. The rms of this sample is only about 1.6 nm. Hexagonal Na_xCoO_2 grains with the six-fold crystal symmetry are clearly observed in both AFM and SEM images. The energy-dispersive x-ray spectroscopy (EDX) measurement along with SEM indicates that the cation ratio of Na:Co in this film is about 0.7:1, which is very close to the result of XRD measurements.

Fig. 3a presents the temperature dependence of the resistivity of $\text{Na}_x\text{CoO}_2/\text{Au}$ multilayers with different Au volume fractions. The resistivities of all samples increase with temperature in the whole temperature range, indicating a metallic-like conducting behavior (i.e., $d\rho/dT > 0$). With the increase of Au volume fraction (or Au layer thickness), the resistivity of the multilayers decreases over the measured temperature range. It needs to mention here that the electrical resistivity of the thin Au layer differs markedly from that of the bulk counterpart. It increases with the decrease of the layer thickness and depends strongly on the layer fabrication process. In this work, the resistivity of the thin Au layer (thickness $\sim 0.5\text{-}12$ nm) is actually much higher than that of the adjacent Na_xCoO_2 layer (for example, the room temperature resistivity of the most conductive 12 nm-thick Au layer is measured to be about 9.7 m Ω cm, which is about 10 times larger than that of Na_xCoO_2). These ultra-thin Au layers could contribute hole carriers to the Na_xCoO_2 matrix and thus lead to a decrease in the electrical resistivity of the Na_xCoO_2 film matrix. Similar doping-like effects have also been obtained in other p-type thermoelectric materials when dispersing

nano-sized metal particles into the thermoelectric matrix [27, 28]. More efforts need to put in to clarify the underlying mechanism in our coming work.

Fig. 4b is the variation of Seebeck coefficient with temperature for $\text{Na}_x\text{CO}_2/\text{Au}$ multilayers with different Au volume fraction. The S value for each sample is positive in the whole measured temperature range, revealing a conduction mechanism in the multilayers mainly governed by holes. Contrary to the significant influence of the thin Au layer on the resistivity of the multilayers, it has little effect on the Seebeck coefficient of the multilayers especially when the volume fraction of Au is less than 17.1% (i.e. the thickness of Au thin layer is less than 8 nm). One hand, the increase in carrier concentration induced by inserting the thin Au layer into Na_xCO_2 matrix will lead to a decrease in Seebeck coefficient S . On the other hand, the very thin Au layer between the Na_xCO_2 layers might result in an enhancement in S due to the quantum-confinement effect, which has already been proved by many theoretical and experimental results. Therefore, the Seebeck coefficient S does not change much. Thicker Au layer or larger Au volume fraction will lead to a significant reduction of the Seebeck coefficient. It might because thicker Au layer, with its resistivity approaching the resistivity of bulk gold, provides another carrier transport pass in the multilayers which was similar to those reported for $\text{Ca}_3\text{Co}_4\text{O}_9$ bulk samples embedded with large Ag particles [29].

The thermoelectric power factor, S^2/ρ , is calculated from measured ρ and S data and is shown in Fig. 4. The power factor of each sample increases with increasing temperature. Appropriate amount of Au can improve power factor of Na_xCoO_2

because it provides a significant reduction of ρ without serious deterioration of S . The $\text{Na}_x\text{CoO}_2/\text{Au}$ multilayer with 17.1 vol.% Au has the best power factor of about 2.0 mW/mK^2 at 800 K, which is about 2.2 times larger than that of the single Na_xCoO_2 layer and is much larger than those reported for Na_xCoO_2 ceramics (power factor~ 0.2-0.6 mW/mK^2 at about 800 K) [22, 30, 31]. We did not obtain the thermal conductivity in ab -plane (k_{ab}) for these multilayers because of the difficulty in measuring k_{ab} for thin film samples with several hundred nanometers. So we can not estimate the ZT value of these multilayers. Nevertheless, if we have a fixed temperature difference and ignore the conversion efficiency, a high-power thermoelectric thin film device could be fabricated using $\text{Na}_x\text{CoO}_2/\text{Au}$ multilayers.

4. Conclusion

In conclusion, $\text{Na}_x\text{CoO}_2/\text{Au}$ multilayers have been grown on single crystal $c\text{-Al}_2\text{O}_3$ substrate by a two-step method. XRD showed that the Na_xCoO_2 layer was c -axis oriented with perfect ab -plane epitaxial growth, and has no Au incorporated into the lattice of Na_xCoO_2 . With the increase of Au volume fraction (i.e. the thickness of Au layer) in the multilayers, the resistivity is remarkably decreased while the Seebeck coefficient is slightly deteriorated when the Au volume fraction is less than about 17.1%. The $\text{Na}_x\text{CoO}_2/\text{Au}$ multilayer sample with the right volume fraction exhibits the best power factor of about 2.0 mW/mK^2 at 800 K, which is about 2.2 times higher than that of the corresponding Na_xCoO_2 single layer. The results demonstrate that the thermoelectric power factor of Na_xCoO_2 can be significantly enhanced in multilayered structures composed of Na_xCoO_2 and metal Au with definite

volume fractions.

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Figure captions:

Fig. 1. (a) XRD θ - 2θ scans of $\text{Na}_x\text{CoO}_2/\text{Au}$ multilayers on $c\text{-Al}_2\text{O}_3$ with different Au volume fractions. From bottom to top, the Au volume fraction is 0, 1.1, 4.4, 8.6, 17.1 and 25.4 vol.%, respectively. (b) ϕ scan of Na_xCoO_2 (103) peak for the sample with Au volume fraction of about 17.1 %. (c) The XPS core-level-spectra of Au 4f for for the sample with Au volume fraction of about 17.1 %.

Fig. 2. AFM and SEM surface images for the Na_xCoO_2 single layer.

Fig. 3. Temperature dependence of (a) resistivity ρ and (b) Seebeck coefficient S for $\text{Na}_x\text{CoO}_2/\text{Au}$ multilayers with different Au volume fractions.

Fig. 4. The dependence of thermoelectric power factor S^2/ρ on temperatures for $\text{Na}_x\text{CoO}_2/\text{Au}$ multilayers with different Au volume fractions.









