Optothermal Raman measurement determined thermal conductivity characteristics in NiMn$_2$O$_4$ films grown by chemical solution deposition

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Keywords: NiMn$_2$O$_4$ alloy, thermal conductivity, Raman

Abstract

NiMn$_2$O$_4$ (NMO) thin films with different thicknesses (0.47–1.90 $\mu$m) were grown on Yttria-stabilized zirconia (YSZ)(100) substrates by chemical solution deposition (CSD). The effects of different growth conditions on the structural and thermal properties of NMO films were investigated. X-ray diffraction (XRD) and atomic force microscopy (AFM) measurements show that both the average grain size of the samples and the surface roughness become larger with an increase of thickness. Based on isothermal surface condition, the corresponding thermal conductivity of NMO films was extracted from the optothermal Raman measurement and the obtained thermal conductivity is $\sim$4.0 ± 0.8 W m$^{-1}$ K$^{-1}$ for micrometer-scale films, suggesting that the (grain) boundary phonon scattering plays a minor role to affect the thermal conductivity of thin NMO films.

1. Introduction

Recently, nickel manganite NiMn$_2$O$_4$ (NMO) with a partially inverse spinel-type structure has drawn considerable attention due to their unusual semiconducting properties and could be used in optoelectronics applications such as batteries [1], solar cells [2] and temperature sensing devices, etc.[3]. Moreover, as a typical negative temperature coefficient thermistor material with a large temperature coefficient of resistance, NMO has been considered as a promising material for uncooled infrared detector application [4], which has the advantages of wide spectral response, low cost and power consumption [5, 6]. Previous studies mainly focused on the growth methods, optical, electrical, phonon, and magnetic properties of NiMn$_2$O$_4$ [7–10]. However, so far, very little research has been devoted to the thermal properties of NiMn$_2$O$_4$. Only Karbi et al [11] measured the thermal conductivity of NMO film grown by spray pyrolysis technique with the help of the photothermal deflection spectroscopy (PDS). The thermal conductivity plays a key role in thermistor films for infrared detector application because the detection efficiency varies inversely with the thermal conductivity ($\kappa$) and thus a reduction of $\kappa$ in NMO can considerably improve their detection efficiencies [5]. Accordingly, it is crucial to characterize the thermal conductivity of NMO films for evaluating their performance as well as revealing the physical nature of heat transport.

The measurement of thermal conductivity of thin films is a challenge because the heat flow cannot be directly measured. As a powerful, in situ and non-contact method, optothermal Raman technique has been developed to investigate the thermal conductivity in micro/nanoscale material systems [12–15]. This technique can avoid both the measurement error caused by the heat flow of contact in the traditional method and additional nanofabrication for materials [16]. Here Raman laser acts as both a heat source and a thermometer at the same time and the thermal conductivity can be determined directly provided that the localized heating...
effects of the laser beam in the sample and the temperature dependence of Raman active phonon mode energy are known [15]. Generally, the thermal conductivity of films increases with the film thickness owing to the phonon boundary scattering reduction [17]. However, for NMO films, depending on the growth conditions and thickness, the grain size and the surface roughness varied with different thicknesses, probably resulting in a different situation. The relationship between thermal conduction and thickness is elusive. On the other hand, the responsive time constant of the thermistor detector is proportional to the heat capacity and thickness of the thermistor film [18]. It means that to get a fast response of the thermistor detector, we have to reduce the thickness of the thermistor film or the heat capacity. Therefore, knowledge of the correlation between the film thickness and thermal conduction would provide useful guidance to design the NMO-based thermistor infrared detector devices.

In this paper, NMO thin films with different thicknesses (0.47–1.90 μm) were successfully grown on Yttria-stabilized zirconia (YSZ) (100) substrates by chemical solution deposition (CSD). The structural and composition properties of all samples were characterized by using X-ray diffraction (XRD) and energy dispersive X-ray spectrometry (EDX) measurement. The thermal conductivity characteristics in NMO thin films are evaluated by the use of optothermal Raman measurement. The influences of laser radius, grain size, surface morphology, and the thickness on the thermal conductivity of NMO films are discussed.

2. Material and methods

NMO thin films were prepared by CSD method. Manganese acetate and nickel acetate were used as raw materials to prepare a precursor solution. According to the molar ratio of Ni: Mn = 1:2, the corresponding proportion of acetate was weighed and dissolved in glacial acetic acid. The precursor solution was filtered through a 0.2 μm syringe filter to remove insoluble impurities. Then, the precursor solution was spin-coated onto YSZ (100) substrates and the wet films were dried at 250 °C for 1 min, then heated at 500 °C for 1 min, following annealed at 750 °C for 5 min, and finally cooled to room temperature in air atmosphere. The annealing temperature of more than 700 °C can lead to the formation of highly crystalline NMO thin film (see figure S1 within the Supplemental Material). However, a higher annealing temperature would result in the formation of the impurity phases of Mn3O4 and MnO2 due to the decomposition of the spinel structure [19]. Thus the optimum annealing temperature is ~750 °C. By repeating deposition and heat treatment, the different thicknesses of the NMO films with 20 layers (20L), 40 layers (40L), 60 layers (60L), and 80 layers (80L) were obtained.

The structure of NMO films was studied by Bruker AXS D8 Discover diffractometer with Cu Kα radiation (λ = 0.15418 nm). The surface morphology, surface roughness, and step height of the films were obtained by Vecco Nanoscope IV atomic force microscopy (AFM) in tapping mode. The cross-sectional images of the NMO films were obtained by FEI Sirion 200 field emission scanning electron microscope (FESEM). Energy-dispersive spectroscopy (EDX) (GENESIS XM, EDAX Corp) was used to analyse the element distribution. Micro-Raman scattering experiments were performed in a quasi-backscattering geometry with 100 × and 10 × microscopes, respectively. The Raman signals excited by a 514.5 nm line of an Ar-ion laser were collected by Princeton tri-vista Raman spectroscopy equipped with a liquid nitrogen-cooled Si-CCD camera. The exposure time is 5 s. The laser power can be adjusted by using neutral density filters. For the temperature dependence Raman measurements, a hot stage was used to heat the sample.

3. Results and discussion

The cross-sectional FESEM images of NMO films are viewed in figure 1. The film thicknesses of sample 20L, 40L, 60L, and 80L are measured as 0.47 μm, 0.92 μm, 1.45 μm, and 1.90 μm, respectively. We found that the film thickness is lineally scaling with the number of layers. To verify precisely the compositions of NMO, EDX measurement was used and the results were illustrated in Figure 2, which indicates the existence of Ni, Mn, and O and the ratio of Ni to Mn is close to 1:2.

Figure 3 gives the XRD pattern of the sample and all characteristic peaks are indexed to cubic spinel structure of NiMn2O4 with space group Fd–3m (PDF card no.04-007-8649). The observed diffraction peaks of NMO can be assigned to (111), (220), (222), (400), (422), (511), (440), which coincide with the data reported in the literature [7, 20].

XRD results reveal that the NMO thin films are polycrystalline. To measure the grain size D of the polycrystalline films, Scherrer equation [21] was used as follow:
where $K$ is the Scherrer constant which is taken as 0.94, $\gamma$ represents the wavelength of X-ray, $L$ is the full width at half maximum of the diffraction peak and $\theta$ is the diffraction angle. The grain size of the samples estimated by Scherrer equation increased from $\sim 35.8$ nm to $\sim 60.4$ nm with an increase of thickness, which is possibly due to longer annealing times for thicker film deposition.

To measure the thermal conductivity, Raman spectroscopy has been proved to be a conventional technique, in which the laser acts as both an excitation source and a heating source simultaneously. Assuming that an approximately isothermal surface condition and the laser beam is a radial Gaussian power density, the surface temperature $T(z = 0)$ for a laser spot of radius $a$ can be derived using [22]:

$$\frac{\partial T}{\partial z} = f(r) = \frac{-Q}{2\pi ak(a^2 - r^2)^{3/2}}, r > 0, z = 0$$
where
\[ T = \frac{Q}{4aT}, \quad \text{thus} \quad \kappa = \frac{Q}{4aT}. \] (3)

For a laser beam with Gaussian distribution and beam waist given as \( \omega \), the total heat flux \( Q \) contained within radius \( r \) on the surface can be calculated as:
\[ Q = P(1 - e^{-2r^2/\omega^2}) \] (4)

The thermal conductivity can be written as following where the laser spot radius \( a \) equals beam waist: [22]
\[ \kappa = \frac{P(1 - e^{-2})}{4aT} \] (5)

In practice, to improve measurement accuracy, a set of measurements with various excitation laser powers was carried out and the equation (5) can be rewritten as:
\[ \kappa = \frac{(1 - e^{-2}) \frac{\partial \Delta k}{\partial T}}{4a \frac{\partial \Delta k}{\partial P}} \] (6)

where \( \kappa \) is thermal conductivity, \( P \) is absorbed laser power, \( a \) is the laser spot of radius, \( \frac{\partial \Delta k}{\partial T} \) and \( \frac{\partial \Delta k}{\partial P} \) are the temperature and laser power dependence of the Raman peak position, respectively. Next, we will show how to determine the thermal conductivity step by step based on equation (6):

(1) The laser absorptivity \( P \)

The absorbed laser powers \( P \) have to take into account the light absorption of the sample. Considering the NMO is a non-transparent material and the absorptivity \( A \) can be obtained as follows:
\[ A = 1 - \left( \frac{n - 1}{n + 1} \right)^2 - k^2 \] (7)

where \( n \) is the refractive index and \( k \) is the extinction coefficient. For the laser with a wavelength of \( \sim 514 \) nm, the values of \( n \) and \( k \) are \( \sim 2.57 \) and \( \sim 0.6 \) for NMO, respectively [9], and then the absorptivity \( A \) was estimated as \( \sim 0.784 \).

(2) The laser spot size \( a \)

The laser beam spot radius, which can be directly measured with a CCD camera, is a critical parameter for the thermal conductivity calculation. The white points in figure 4 are laser beam spot size data under a \( 10 \times \) objective taken from the CCD camera images. The red curves are fits to the Gaussians and the laser beam radius on the sample is determined as \( \sim 11.2 \) \( \mu \)m and \( \sim 28.1 \) \( \mu \)m for both \( x \) and \( y \) directions, respectively. Thus the average size of the laser beam radius \( a \) is \( \sim 17.8 \) \( \mu \)m. Under \( 100 \times \) objective with a high numerical aperture (NA), the corresponding focused laser beam radius \( a \) is reduced to \( \sim 1.8 \) \( \mu \)m (not shown here), which is only \( \sim 10\% \) of that under \( 10 \times \).
(1) Temperature-dependent Raman spectra: $\frac{\partial \Delta k}{\partial T}$

Figure 5 shows the temperature-dependent Raman spectra of MNO films with a thickness $\sim 1.9 \ \mu\text{m}$. Two dominant Raman lines are well detected. The $\sim 515 \ \text{cm}^{-1}$ peak is designated as the $F_{2g}$ vibration mode corresponding to a Ni-O stretching mode. The stronger peak located $\sim 650 \ \text{cm}^{-1}$ is attributed to the $A_{1g}$ vibration mode, which represents the symmetric Mn-O stretching vibration involving the movement of the oxygenates within the octahedral MnO$_6$ [10]. With an increase of temperature, both $F_{2g}$ and $A_{1g}$ modes shift to the left (red-shift) linearly due to the thermal expansion effect. The Raman peak position ($\Delta k$) versus temperature ($T$) is also plotted in figure 4(b), which shows a good linear relationship with fitted slope $\frac{\partial \Delta k}{\partial T} = -0.056 \ \text{cm}^{-1} K^{-1}$. Based on the temperature dependence of Raman spectra, the localized temperature rise can be deduced accurately.

(1) Power-dependent Raman spectra: $\frac{\partial \Delta k}{\partial P}$
These local variations in thermal conductivity might arise from the local change of the absorbed laser power caused by the roughness of the surface and shows a porous interior, leading to the strong variations in thermal conductivity when the 100 μm radius of the samples increased monotonically with an increase of thickness. The measured thermal conductivities together with the grain sizes calculated by Scherrer equation are listed in table 1. The obtained thermal conductivities are comparable to the surface asperities, strong variations in the thermal conductivities are expected. The obtained thermal conductivities κ of the film (~1.90 μm) by the Raman shift experiment under 100 μm objective are in the range between ~1.6 and ~3.2 W m⁻¹ K⁻¹, depending on the laser spot position. We attribute the local strong variations in κ observed in this material to the surface structural features.

To get the thermal conductivity of the film rather than the local thermal conductivity, a larger laser beam radius a is preferred. Here we use 10 μm objectives with a laser beam radius a ~17.8 μm and the yielded thermal conductivity together with the grain sizes calculated by Scherrer equation are listed in figure 8 which displays that the grain size of the samples increased monotonically with an increase of thickness. The measured thermal conductivity under 10 μm objective is ~4.0 ± 0.8 W m⁻¹ K⁻¹. For Raman thermal conductivity measurements, there exists both error and uncertainty. The error arising from the inadequacy of the thermal model which perfectly describes the temperature distribution is suggested to be less than ~5% [25]. According to equation (5), the uncertainty in Raman thermal conductivity measurement is mainly from the measurement of laser power P, laser spots size a and the temperature T. The laser spot size a was estimated as ~17.8 μm with an accuracy of ~0.5 μm, which produces additional uncertainty of about ~3%. The measurement of laser power P produces uncertainty of about ~2%. Depending on the sample, the thermal conductivity uncertainty is the order of ~5%–10% determined by the experimental reproducibility of the temperature T. In a word, errors of ~5% coupled with uncertainties of

The laser-power-dependent Raman spectra of NMO thin films under 10 × are displayed in figure 6. It was found that the A1g modes tend to shift toward lower wavenumber as the laser power increases. We have shown that the redshift of A1g modes mode is due to the thermal effect as temperature increases (see figure 5). Thereby, it can be considered that the redshift of the Raman peak introduced by laser power arises from the temperature change caused by local laser heating and the local temperature of the sample surface becomes higher under a higher laser power. It is clearly observed that the Raman shift (Δκ) linearly depends on the laser power (P) with slope (Δκ/ΔP) = ~1.35 cm⁻¹ mW⁻¹ (0.47 μm), ~1.42 cm⁻¹ mW⁻¹ (0.92 μm), ~1.30 cm⁻¹ mW⁻¹ (1.45 μm) and ~0.13 cm⁻¹ mW⁻¹ (1.90 μm), respectively.

When the value of P, a (Δκ/ΔP) and (Δκ/ΔP) are given, the thermal conductivity κ can be evaluated according to equation (6). We have mentioned that under 100 × and 10 × objective, the corresponding focused laser beam radius a are ~1.8 μm and ~17.8 μm, respectively. Once the laser beam radius a is comparable to the surface asperities, strong variations in the thermal conductivities are expected. The obtained thermal conductivities κ of the film (~1.90 μm) by the Raman shift experiment under 100 × objective are in the range between ~1.6 and ~3.2 W m⁻¹ K⁻¹, depending on the laser spot position. We attribute the local strong variations in κ observed in this material to the surface structural features.

To take a closer look into the surface morphology of the films, AFM images were taken as in figure 7, which shows that the RMS roughness of the films become larger with an increase of thickness and are estimated as ~5.2 nm, ~7.0 nm, ~11.4 nm, and ~13.5 nm, respectively. It was further confirmed by the corresponding typical height profile plotted in figure 7(f). For the thick film (~1.90 μm), the surface of this feature is more pronounced and shows a porous interior, leading to the strong variations in thermal conductivity when the 100 × is employed, reflecting that the Raman shift method is able to detect the local variations of the thermal conductivity in microscale. These local variations in thermal conductivity might arise from the local change of the absorbed laser power caused by the roughness of the surface [15, 23, 24].

Figure 6. Power-dependent Raman spectra of NMO films. The black dashed lines are a linear fit for peak position as a function of laser power.
∼10%–15% are attainable by optothermal Raman measurement. To be on the safe side, we set the final standard deviation in the calculation of $\kappa$ by Raman the order of ∼20%.

This value is much less than 25 W m$^{-1}$ K$^{-1}$ reported by Karbi et al [11] for NMO thin films measured by photothermal deflection spectroscopy technique. This difference may be attributed to the different sample preparation methods and test approaches.

In general, the thermal conductivity of semiconductors increases with the film thickness due to the reduction of the phonon boundary scattering [17, 26]. Moreover, given the fact that the NMO films were polycrystalline, it is known that thermal conductivity can be significantly reduced by increasing the grain boundary phonon scattering as a result of decreasing the grain size [27, 28]. However, in this work, the measured thermal conductivity almost maintained constant independent of the film thickness and the grain size which is rather smaller than the film thickness, suggesting that the effective phonon mean free path is much less than the grain size [29, 30].

4. Conclusion

In this work, NMO thin films with thickness varying from ∼0.47 to ∼1.90 μm were successfully synthesized on YSZ (100) substrates by CSD method. With an increase of thickness, both the grain size and the surface asperities increase as well. The thermal conductivity of NMO films was determined by optothermal Raman method based on an approximately isothermal surface condition. Irrelevant to the film thickness and the grain size, the derived thermal conductivity is kept nearly constant as ∼4.0 ± 0.8 W m$^{-1}$ K$^{-1}$, indicating that thermal conductivity mainly arises from the alloy phonon scattering rather than (grain) boundary scattering. Moreover, care should be excised when the optothermal Raman method is employed to estimate the thermal conductivity of the thin
film with the large surface asperities: to obtain the thermal conductivity instead of the local thermal conductivity of the film, a larger laser beam radius should be considered.

Acknowledgments

D C X and Y X S contributed equally to this work. This work is supported by the National Natural Science Foundation of China (Grant No. 11874377), Natural Science Foundation of Shanghai (Grant No. 18ZR1445700).

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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