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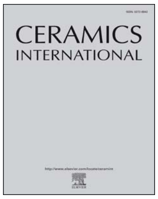

Enhanced bolometric properties of nickel oxide thin films for infrared image sensor applications by substitutional incorporation of Li

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ABSTRACT

This study aims to investigate the influence of substitutionally incorporated Li on sensing performance of nickel oxide films for bolometer applications by comparing $Ni_{1-x}O$ and $(Li_yNi_{1-y})_{1-x}O$ films. From the results of structural analysis, it was confirmed that the film deposited from $Li_{0.2}Ni_{0.8}O$ target contained Li which substitutionally occupies the Ni cation site while maintaining a cubic NiO structure. The substitutionally incorporated Li in nickel oxide can serve as an acceptor providing a hole carrier, like as a structural defect. However, in contrast to the structural defect, the substitutional incorporation of Li made it possible to increase the number of hole carriers in nickel oxide film while maintaining excellent film quality. In addition, the contact resistance with electrode was greatly reduced as a result of the substitutionally incorporated Li. These changes in structural and electrical properties lead to a significant reduction of $1/f$ noise arisen from the $(Li_yNi_{1-y})_{1-x}O$ film. As a result, the sensing performance of the $(Li_yNi_{1-y})_{1-x}O$ film as evaluated using the $(\alpha_H/n)^{1/2}/|\beta|$ value was nearly 10 times better than that of the $Ni_{1-x}O$ film. Consequently, it can be concluded that the substitutional incorporation of Li can significantly improve the sensing performance of nickel oxide films for bolometer applications.

1. Introduction

A bolometer is a thermal-type infrared detector which senses the radiation-induced temperature rise via changes in the electrical resistance of the sensing material. The temperature resolution of a bolometer, which indicates how small a temperature difference the device can distinguish, is determined by the properties of the sensing material. Therefore, to achieve excellent sensing performance, it is essential to use a material with a high temperature coefficient of resistivity (TCR), high electrical conductivity, and low $1/f$ noise characteristics [1–3]. Thus, to find an appropriate sensing material for bolometer applications, extensive studies have been conducted on a variety of materials, such as metals [4,5], semiconductors [6–9], and superconductors [10,11].

Nickel oxide thin film, a typical p-type semiconductor, is an attractive material for a variety of applications based on its interesting electrical and optical properties and its excellent chemical stability [12]. Furthermore, it has recently been considered as a promising alternative material to replace commercial sensing materials such as vanadium oxide (VO_x) and amorphous silicon (a-Si) [13,14]. Therefore, a number of research efforts have been made to confirm the feasibility of nickel oxide film as a sensing material and to improve its performance. In our previous studies, we found that the sensing performance of nickel oxide films deposited by the RF magnetron sputtering method was affected by conditions under which the film samples were grown. We also reported that the best sensing performance was obtained from a film with a TCR value of $-2.76\%/K$ and a normalized Hooge parameter (representing the magnitude of the $1/f$ noise) of 2.40×10^{-27} m^3 [15,16]. Although nickel oxide film can overcome the problems of commercial materials based on its CMOS compatibility, good reproducibility, and easy processability, it provides similar or slightly lower sensing performance than VO_x due to its relatively large amount of $1/f$ noise [7,8,17]. Therefore, in order to improve the feasibility of nickel oxide film as an alternative sensing material, it is necessary to devise a type of nickel oxide film which offers better sensing performance capabilities.

Recently, several research groups reported that the performance of nickel oxide films in various applications can be increased by improving the structural as well as electrical properties through substitutional incorporation of monovalent atoms such as Li, Na, and K [18–20]. The ionic radius of Li ($r_{Li+} \approx 0.68$ Å) is most similar to the Ni^{2+} cation ($r_{Ni2+} \approx 0.69$ Å) among the other monovalent atoms [21]. Therefore,

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Li, which can minimize structural distortion, is mainly used as an incorporated atom [22,23]. Moulki et al. [24] revealed that the electrochromic performance of the nickel oxide film can be improved via substitutionally incorporated Li. Other authors also reported that the nickel oxide film in which some of Ni sites are substituted by Li ($(Li_yNi_{1-y})_{1-x}O$) can exhibit better thermoelectric performance levels [25] and hydrogen sensing performance capabilities [18] than typical nickel oxide film ($Ni_{1-x}O$). Moreover, numerous studies have been conducted on $(Li_yNi_{1-y})_{1-x}O$ films used for transparent conductive oxides [26–28], dye-sensitive solar cells [21], and UV detectors [29]. However, to the best of our knowledge, no attempts have been made to use $(Li_yNi_{1-y})_{1-x}O$ film as an infrared sensing material for bolometer devices.

Therefore, in this study, we attempt to obtain a comprehensive understanding of the effect of substitutionally incorporated Li on the sensing performance of nickel oxide films for bolometer applications by systematically analyzing and comparing the structural and bolometric properties of $Ni_{1-x}O$ and $(Li_yNi_{1-y})_{1-x}O$ films. We expect that these results can provide a new approach to improve the performance capabilities of bolometer devices using transition-metal oxides as an infrared sensing material.

2. Experimental details

$Ni_{1-x}O$ and $(Li_yNi_{1-y})_{1-x}O$ films were deposited by RF magnetron sputtering onto SiO_2/Si substrates using Ni and $Li_{0.2}Ni_{0.8}O$ targets, respectively. The target-to-substrate distance was fixed at 138 mm and the incident angle was approximately 45° to the normal surface of the substrate (off-axis). The process chamber was evacuated to a base pressure below 5×10^{-7} Torr using rotary and turbo molecular pumps, after which high-purity Ar and O_2 gases were introduced into the chamber. The flow rate of each gas was adjusted by means of an individual mass flow controller (MFC) under a constant total flow rate of 25 sccm. The deposition process was carried out under different oxygen fractions in an $(Ar+O_2)$ gas mixture for the $Ni_{1-x}O$ films and under an Ar gas atmosphere for the $(Li_yNi_{1-y})_{1-x}O$ film. The sputtering pressure and power were kept at 1 mTorr and 300 W, respectively, and no intentional substrate heating was performed during the deposition process. Prior to each deposition step, a pre-sputtering process was conducted for 30 min under an Ar atmosphere to eliminate any contamination on the target surface.

The thickness of the deposited films was measured using a spectroscopic ellipsometer (M2000D model, Woollam). The chemical binding states and compositions of the films were analyzed by X-ray photoelectron spectroscopy (K-Alpha model, Thermo VG scientific) using an Al Kα radiation source ($h\nu = 1486.6$ eV). Before the measurement, the films were sputter-cleaned with low energy Ar^+ ions to remove any surface contaminant. The acquired spectra were corrected by referencing the Ar 1s peak (241.9 eV) for compensation of the charging effect. Inductively coupled plasma optical emission spectroscopy (ICP-OES 720 model, Agilent) was utilized to identify the Li element and determine the quantitative chemical concentration, and an X-ray diffractometer (D/MAX 2500 model, Rigaku) with a monochromatic Cu Kα radiation source ($\lambda = 1.5418$ Å) was employed to characterize the crystallographic structure of the deposited films.

To investigate the bolometric properties of the deposited $Ni_{1-x}O$ and $(Li_yNi_{1-y})_{1-x}O$ films, bar pattern devices were fabricated using standard lithographic techniques via the following steps: first, silicon oxide (100 nm) was deposited as a hard-mask layer onto the $Ni_{1-x}O$ or $(Li_yNi_{1-y})_{1-x}O$ film sample by means of plasma-enhanced chemical vapor deposition. Silicon oxide and nickel oxide films were then sequentially etched with a buffered oxide etchant (B.O.E.) and with an HCl solution, respectively. To ensure good electrical contact, the silicon oxide film was removed, except for the center area (50 μm × 50 μm), which is utilized as a passivation layer. Finally, Cr (5 nm) and Au (100 nm) were sequentially deposited as electrode materials by a thermal evaporation technique and then patterned by a wet-etching process. A schematic diagram of the device is depicted in Fig. 1.

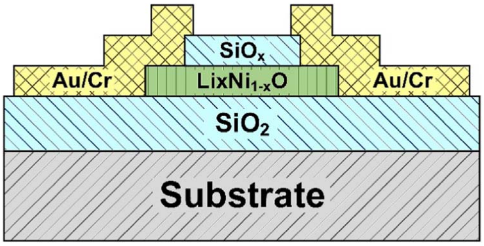

Fig. 1. Schematic diagram of a fabricated device.

The electrical conductivity and specific contact resistance were extracted by current-voltage (*I-V*) measurements via a parameter analyzer (HP4156C model, Hewlett Packard) and a probe station. The activation energy and TCR values were calculated from the temperature dependence of the resistivity as obtained from the *I-V* behaviors measured while varying the device temperature from 283 K to 340 K using a thermo-electric cooler (TEC) system. In addition, the noise characteristics were measured under various bias conditions using a low-noise amplifier (SR570 model, Stanford Research Systems) and a dynamic signal analyzer (SR780 model, Stanford Research Systems) in the frequency range of 1–100 Hz.

3. Results and discussion

3.1. Structural properties

Fig. 2 shows the XPS survey spectra as well as the high-resolution XPS spectra of the Li 1s region (see inset) for all of the deposited films. In contrast to $Ni_{1-x}O$ films in which only peaks related to nickel and oxygen are observed, it can be confirmed that the film deposited from the $Li_{0.2}Ni_{0.8}O$ target contains lithium as well as nickel and oxygen. Moreover, it was found that no peak could be detected at the binding energies associated with metallic Li (~52.3 eV) or interstitial Li (~53.0 eV), whereas only one peak was clearly observed at around 54.2 eV, corresponding to substitutional Li [30–32]. These findings imply that Li incorporated into the film deposited from $Li_{0.2}Ni_{0.8}O$ target substitutionally occupies only the Ni site and does not create an interstitial Li defect.

The chemical compositions of the films calculated from the high-resolution XPS spectra, in this case Ni $2p_{3/2}$, O 1s and Li 1s are summarized in Table 1. This table shows that the $Ni_{1-x}O$ films contain more O atoms than Ni atoms. The *x* value in $Ni_{1-x}O$, which represents the nickel deficiency value, increases from 0.039 to 0.106 as the oxygen fraction increases from 20% to 80%. The excess oxygen in the nickel oxide film caused by the Ni deficiency creates structural defects via the following reactions [33]:

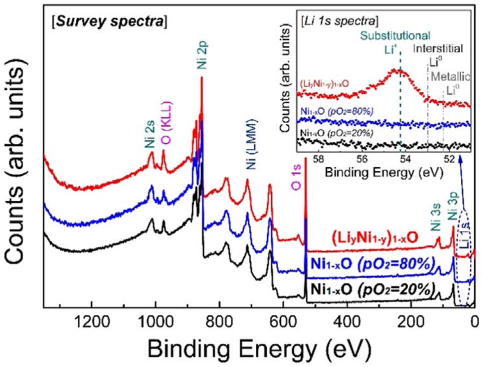

Fig. 2. XPS survey spectra of all deposited films (Inset: High-resolution XPS spectra of the Li 1s region).