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Dielectric properties of $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ thin films measured by Fourier transform infrared spectroscopy

Yi-Chun Chen [a], Hsiang-Lin Liu [a], Hsiu-Fung Cheng [a,*], I.-Nan Lin [b]

[a] Department of Physics, National Taiwan Normal University, Taipei 117, Taiwan, ROC
[b] Materials Science Center, National Tsing-Hua University, Hsinchu 300, Taiwan, ROC

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Abstract

We report the far infrared measurement for comparing the dielectric properties of $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$, BiZN, thin films and bulk ceramics. The dielectric constants obtained by extrapolating the IR properties to the microwave frequency region for the thin films $(\varepsilon_1)_{film} = 20$ is markedly smaller than those for bulk ceramics. The frequency response, measured by Fourier transform infrared spectroscopy (FTIR), reveals that the phonon peaks of BiZN thin films occur at higher frequencies and have smaller amplitudes, as compared to those of BiZN bulk. This phenomenon implies that the smaller dielectric constant for BiZN thin films is due to the strain induced in the thin films.

Keywords: Dielectric properties; Films; FTIR; Microwave ceramics

1. Introduction

Microwave dielectric thin films possess overwhelmingly advantages over bulk materials in several aspects, including lower operation voltages, faster response and, most of all, a nonlinear relationship in dielectric properties,[1,2] which provides the tunability for the devices. Therefore, applications of these thin films as planar capacitors, coplanar waveguides, tunable phase shifters, tunable mixers and tunable filters have been extensively investigated.[3] Recent investigations indicate that Bi_2O_3–ZnO–Nb_2O_5 series materials[4,5] exhibit marvelous properties such as high dielectric constant, low dielectric loss, and an adjustable temperature coefficient of resonance frequency.

However, dielectric properties of thin films are usually inferior to those of bulk materials of the same composition. To understand such a phenomenon, comparing the dielectric properties of the two forms of materials at the same operating frequency is necessary. Fourier Transform Infrared Spectroscopy (FTIR) has become a powerful tool[6] for estimating the dielectric properties of materials in the microwave frequency region and was thus adopted to study the microwave dielectric properties of thin films and bulk BiZN materials. The probable mechanism, which degrades the characteristics of thin films, is discussed.

2. Experimental methods

$Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$, BiZN, ceramic materials were prepared by a conventional mixed-oxide process including mixing, calcining, pulverizing, pelletizing and then sintering at 1100°C for 4 h. The BiZN thin films were prepared by a pulsed laser deposition (PLD) technique,[7] using a pulsed XeCl excimer laser ($\lambda = 308$ nm, Lambda Physik) with an energy density of 3 J/cm^2. The films were deposited on Si substrate at 400–600°C in 0.1 mbar oxygen pressure (Po_2), followed by 10 min of annealing at the depositing temperature under 1 atm Po_2. The phase constituent was examined using an X-ray diffractometer (Rigaku, Dmax/IIB). The microwave dielectric properties of the bulk ceramic materials were measured by a parallel plate dielectric rod resonator method[8] using an HP 8722 network analyzer.

In infrared spectroscopy, far-infrared transmittance was measured using a Fourier transform infrared spectrometer

* Corresponding author. Tel.: +886-2-293-31075; fax: +886-2-293-26408.
E-mail address: hfcheng@phy03.phyntnu.edu.tw (H.-F. Cheng).

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PERKIN-ELMER System 2000, which possesses a resolution of 4 cm^{-1}. In addition, the reflectance measurements of bulk materials were performed over a wide frequency region between 200 and 1200 cm^{-1} using the deposited aluminum as a reference. The transmittance spectrum of the films were analyzed using the Lorentz model,[9] whereas the reflectivity spectrum, analyzed using Kramers–Krönig (K–K)[9] relation for the real and imaginary parts of the dielectric constant.

3. Results and discussion

The X-ray diffraction (XRD) patterns shown in Fig. 1 reveal that the BiZN films are readily crystallized, forming pyrochlore BiZN phase, for a substrate temperature of 600°C. The crystallinity of the films varies with deposition temperature significantly and are [222] preferentially oriented when deposited at 600°C. The relative volume fraction of [222] oriented grains was estimated from the integral intensity of diffraction peaks in XRD patterns by using the formula:

$$X_{222} = \frac{(I_{222})_0}{\sum_{hkl}(I_{hkl})_0} \qquad (1)$$

where $(I_{hkl})_0$ is the normalized integral intensity of the [*hkl*] diffraction peak. The normalized integral peak intensity is defined as the ratio of measured I_{hkl} for the thin films and those for the randomly oriented materials, which were polycrystalline BiZN targets. The proportion of grains oriented in [222] direction for BiZN film synthesized at 600°C is about 73%.

The transmitted spectra of the BiZN thin films, measured in the range of 200–700 cm^{-1} operating wavenumber, are shown in Fig. 2(a), which indicates that the transmittance T of the crystalline BiZN/Si films is about 15–25% in far infrared region. The transmission minimums occur at 320, 510 and 600 cm^{-1}, which imply the existence of phonons. The dielectric properties of the films can be analyzed from the transmission spectra using the Lorentz model.[9] According to the dispersion theory, the real part and the imaginary part of the dielectric constant, ε_1 and ε_2, which are functions of frequency, are given by:

$$\varepsilon_1 = \varepsilon_\infty + \sum_i \left(\frac{4\pi e^2 N_i}{mV}\right) \cdot \frac{\left(\omega_{0i}^2 - \omega^2\right)}{\left(\omega_{0i}^2 - \omega^2\right)^2 + \gamma_i^2\omega^2} \qquad (2)$$

$$\varepsilon_2 = \sum_i \left(\frac{4\pi e^2 N_i}{mV}\right) \cdot \frac{\gamma_i \omega}{\left(\omega_{0i}^2 - \omega^2\right)^2 + \gamma_i^2\omega^2} \qquad (3)$$

where ω_{0i} is the resonance frequency, γ_i is the damping coefficient, ε_∞ is the dielectric constant caused by the electronic polarization at high frequencies, N_i is the number of charges bound with resonance frequency ω_{0i}, and the summation is over the i resonances in the spectrum. The measured transmission data are fitted to obtain the dispersion parameters of BiZN thin films, taking into account the transmittance and reflectance at interfaces. Fig. 2(a) illustrates that the transmittance calculated from the analyzed dielectric response of the films fit with the measured transmittance very well.

Fig. 2(b) shows the reflectance spectra for BiZN bulk, on an x-logarithmic scale. The reflectance, R-value, approximates to a constant of about 0.2 at wave-

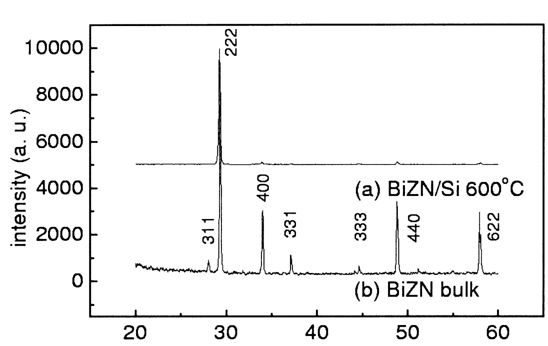

Fig. 1. X-ray diffraction patterns of (a) BiZN thin films deposited on Si at 600°C (b) BiZN bulk material.

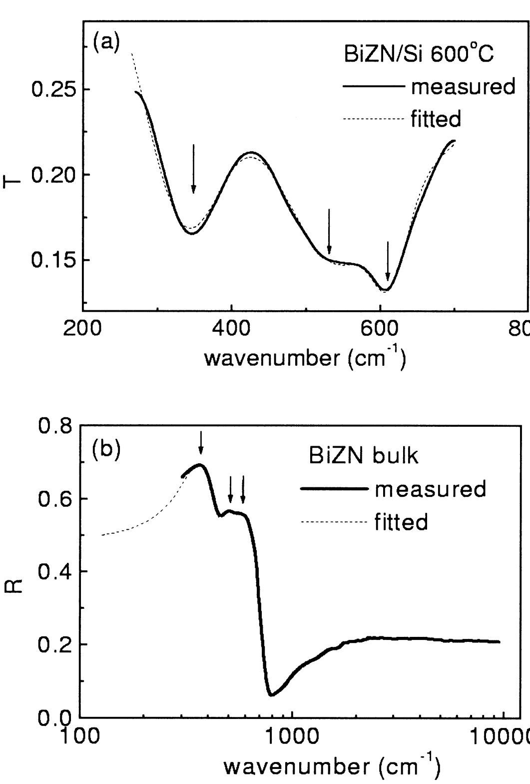

Fig. 2. (a) Far infrared transmittance spectra for BiZN thin films deposited on Si at 600°C and (b) far infrared reflectance spectra for BiZN bulk material.

numbers higher than 2000 cm^{-1}, indicating that the phonon peaks are mostly located in the far infrared regime and none exist in the large wavenumber regime. Reflectance maximums in Fig. 2(b) reveal the resonant modes of the lattice vibrations that occur around 350 and 500 cm^{-1}. K–K analysis[9] is performed to calculate the dielectric properties of the films. Fig. 2(b) also reveals that the reflectivity calculated from the K–K analysis (dash line) fits the measured reflectivity (solid line) very well.

Fig. 2(a) and (b) reveals that the phonon modes of BiZN bulk materials are similar to those of thin films, except that the resonance peaks of thin films shift to higher frequencies (illustrated by arrows). The shift of phonon peaks in thin films suggests that the compressive strain is induced, probably by the lattice mismatch between Si substrate (4.8 Å) and BiZN material (10.5 Å).

The dielectric constant (ε_1) of BiZN thin films analyzed from transmission spectrum and that of BiZN bulk materials analyzed by the Kramers-Krönig relation are shown in Fig. 3(a) and (b), respectively. The ionic polarization is assumed to be the most important mechanism determining the dielectric properties in microwave frequency region. Since normal mode lattice vibrations, which cause ionic dipole polarization, usually exist in far infrared region only, the dielectric properties at microwave frequencies can be estimated by extrapolating the dielectric response from the far infrared measurement to the lower frequency regime. Fig. 3(a) reveals that the extrapolated static dielectric constant $\varepsilon_{1\text{-film}}(0)$ of BiZN thin films is 20, which is contributed from the lattice vibrations at infrared frequencies 345, 534 and 608 cm^{-1}. By contrast, the static dielectric constant $\varepsilon_{1\text{-bulk}}(0)$ of the BiZN bulk is 32 [Fig. 3(b)], which is contributed from lattice vibration at slightly smaller frequencies, viz. 308, 485 and 567 cm^{-1}. Moreover, the resonance peaks occurring at 500–600 cm^{-1} (Fig. 3) also reveal that the damping coefficient γ of thin films is lower than that of bulk materials, and the recognition of two peaks implies the better crystallinity of the films.

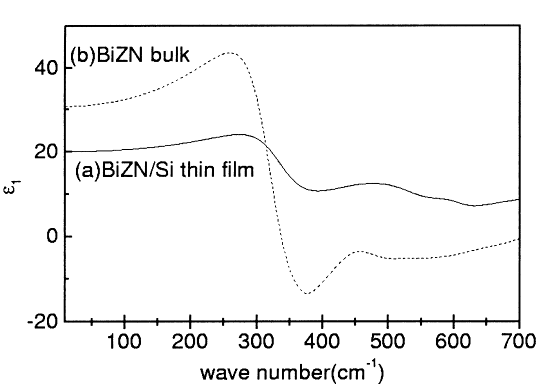

Fig. 3. Dielectric constant calculated from infrared spectra of (a) BiZN thin films deposited on Si at 600°C and (b) BiZN bulk material.

It is interesting to observe that the dielectric constant of the BiZN thin films is markedly smaller than that of BiZN bulk ceramic in the microwave frequency region. Smaller dielectric constants for the BiZN thin films, when compared with those for the bulk BiZN materials can apparently be accounted for by the smaller grain size of the thin film materials. Microstructure examinations indicate that the grains of the BiZN films are very small (~0.3 μm), on the other hand, the grains of BiZN bulk materials are very large (~10 μm). The films contain a large proportion of grain boundaries, which is expected to result in highly disordered characteristics. Moreover, the films are generally strained due to mismatch in the lattice parameters between BiZN materials and the Si substrates, which may also induce lower dielectric constant.

4. Conclusions

BiZN thin films were prepared by a pulsed laser deposition process on Si substrates. The reflectance and transmittance measurements of BiZN bulk materials and thin films, respectively, are performed in the far-infrared range. The dispersion parameters analyzed by Kramers–Krönig relation or Lorentz model were used to extrapolate the dielectric properties of BiZN bulk and thin film materials to low frequencies. The estimated dielectric constant in the microwave frequency region, $(\varepsilon_1)_{bulk} = 32$, is close to the dielectric constant measured by parallel plate method ($(\varepsilon_1) = 65$). The ε_1 value of BiZN thin film, $(\varepsilon_1)_{film} = 20$, is pronouncedly smaller than that of bulk material. This phenomenon can be accounted for by the strain induced in BiZN thin films due to the interaction between the film and the Si substrate.

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