ナノスケールの層状酸化物を用いた透明断熱薄膜の設計

Design of Transparent Thermal Insulating Thin Films of Nanoscale-layered Oxides

○呉　彦儒（物材研）　徐 一斌（物材研）
○Yen-Ju WU* and Yibin XU**
* International Center for Young Scientists (ICYS), National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
** Research and Services Division of Materials Data and Integrated System (MaDIS), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
Corresponding author: Yen-Ju WU, E-mail: Wu.YenJu@nims.go.jp

In industrial application, one of the important features for thermal insulating films in electronic devices is transparency. In order to expand the potential for industrial application, both high transparency and thermal insulating performance must be pursued. For discovery of the material systems which satisfy both properties, the extrapolative search by adaptive learning is applied combining with the previous proposed ITR model. The reduction in thermal conductivity is related to the high density of interfaces which have high ITR rather than to the change of intrinsic thermal conductivity. The consistent thermal conductivity of TiO_2 of 1.56 W/mK from 5 nm to 50 nm is observed. The selected material system of SiO_2/TiO_2, nanoscale-layered thin films synthesized by sputtering, show ultra-low thermal conductivity of 0.21 W/mK and high transparency (>90%, 400-780 nm). The strong substrate dependence is also found that the additional Ti_2O_3 phase forms as growing on Si substrate and reduces the thermal resistance as relative to the one on quartz glass substrate. Compared to the current transparent thermal insulating materials, aerogel or polypropylene, the proposed SiO_2/TiO_2 composites have higher transparency, higher robusticity, good adaptivity to electronics, and lower cost.

1. Introduction

The transparent thermal insulating materials have been used for wide applications in decreasing heat losses and increasing efficiency for clean energy usages such as thermal collectors. The low thermal conductivity and high transmittance are two essential properties, and the ability to reduce heat losses and to provide high transmittance varies depending on material types and operating temperature. The nanocomposite structure by introducing the periodic multilayers has provided an effective strategy to reduce the thermal conductivity, even lower than that of homogeneous amorphous structure and the theoretical predicted values. The phonon propagation in such structures is hindered by scattering into random directions or associated interferences when they encounter interfaces in nanostructured materials. Various methods to identifying candidates which have high interfacial thermal resistance (ITR) have been proposed, such as the acoustic mismatch model, the diffuse mismatch model, and molecular dynamics.[1] Although these models assist in evaluating the ITR of material systems, they fail in a large-scale prediction or large mismatch between simulation and prediction. Another approach to predicting the ITR by machine learning model which includes chemical, physical, and process factors with higher predictive performance to select the materials from among hundreds of thousands of systems was proposed in our previous work. [2] The combination of a machine learning prediction model and an interface design enable the realization of nanocomposite thin films with low thermal conductivity. [2]

The high transmittance is another main issue to be addressed toward the transparent thermal insulating materials. For discovery of the material systems which satisfy both properties, the searching space for materials candidates should be confined to transparent materials with larger band gap. However, approximately 95% data in our ITR database are metal/nonmetal which are not transparent, resulting in small overlap between the training data and searching space. Therefore, the extrapolative search by adaptive learning will be applied combining with the previous proposed ITR model.

2. Experimental Procedure

2.1 Film deposition

The samples of TiO_2/SiO_2 layered thin films were prepared on quartz glass (Qz) or Si substrates in a sputtering system (CFS-4EP-LL, Shibaura Mechatronics Corp.) at a pressure of around 6×10^{-5} Pa before deposition. The pressure was maintained at 0.4 Pa (Ar flow of 20 sccm) during the deposition process. Ar was used as the sputtering gas for Au at 20 sccm, whereas both Ar and O_2 were applied for TiO_2 (Ar:16 sccm,

O_2:4 sccm) and SiO_2 (Ar:13 sccm, O_2:13 sccm). The RF power was set at 200 W for both TiO_2 and SiO_2, whereas the DC power was at 50 W for Au. Parameters TiO_2:SiO_2 are the thickness of TiO_2 and SiO_2 corresponding to the quartz crystal resonator; the thicknesses of TiO_2 and SiO_2 were increased from 1, 5, to 30 nm, as shown in Table 1. After the TiO_2/SiO_2 deposition, a 120 nm-thick Au layer was deposited, without evacuation, at the top as a heat absorber for thermal measurement. The total film thickness and the thickness of each layer was analyzed using transmission electron microscopy (TEM, JEM-ARM200F, JEOL Ltd.). The structural properties of the thin film were characterized using X-ray diffraction (Smartlab, Rigaku Corp.)

Table 1 Experimental parameters of samples

Sample	TiO_2:SiO_2	Substrate
TS-Qz-30	30:30	Qz
TS-Qz-5	5:5	Qz
TS-Qz-1	1:1	Qz
TS-Si-30	30:30	Si
TS-Si-5	5:5	Si
TS-Si-1	1:1	Si

2.2 Heat conduction equation

The thermal resistance measurement was performed by using frequency-domain thermoreflectance (FDTR).[3] The thermal resistance was along the perpendicular direction (cross-plane) to the Qz or Si substrate. The heat conduction was assumed to be one-dimensional due to the laser spot being much larger than the film thickness, as shown in eq. (1).[4]

$$\frac{T(0)}{qd_0} = \frac{e^{-i\frac{\pi}{4}}}{\sqrt{2\omega\lambda_3 C_3}} + R_0 + \left(1 - \frac{\lambda_2 C_2}{\lambda_3 C_3}\right)\frac{d_2}{\lambda_2} + \left(1 - \frac{\lambda_1 C_1}{\lambda_3 C_3}\right)\frac{d_1}{\lambda_1} + \left(\frac{1}{2} - \frac{\lambda_0 C_0}{\lambda_3 C_3}\right)\frac{d_0}{\lambda_0} \quad .(1)$$

Where, $T(0)$ is the temperature of the Au, q is heat per unit volume, C is heat capacity per unit volume and λ is thermal conductivity. R_0 is the sum of interfacial thermal resistances at Au/SiO_2, SiO_2/TiO_2, and TiO_2/substrate. The subscript 0, 1, 2 and 3 denote the Au, TiO_2, SiO_2 and substrate, respectively. The temperature on the surface of the Au film, $T(0)$, was detected by a thermoreflectance method using a probe laser with applying an alternating current of a frequency of ω. If we plot $\frac{T(0)}{qd_0}$ versus $\omega^{-1/2}$, the intercept gives the sum of the last four terms of eq. (1). With the known thickness, the specific heat and thermal conductivity of the Au, SiO_2 and TiO_2 films and substrate, the second term of R_0 can be calculated.

3. Results and Discussion

3.1 Data-driven materials selection

Firstly, the proposed ITR machine learning model[2] was applied to select the transparent interface with high ITR. From our ITR database as shown in Fig. 1, most of the data are nontransparent or semi-transparent, while the transparent data is less than 5%. The ITR database are available in our previous work.[5] The nontransparent data represents the two materials aside the interface are both nontransparent, and the semitransparent data are the interface which includes one transparent material. Due to the large mismatch between the training data of ITR database and the searching space of transparent interfaces, which may result in high uncertainty of the prediction, the extrapolative search by adaptive learning with Bayesian optimization (COMBO)[6, 7] and experimental validation was performed.

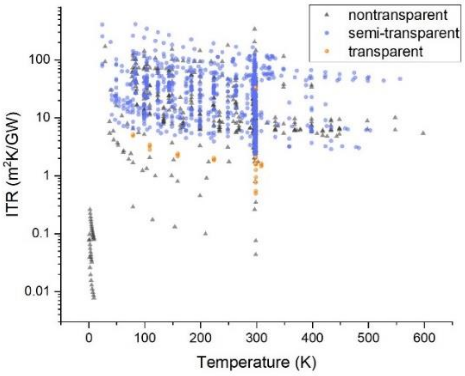

Fig. 1 Relationship between the ITR and temperature.

The transparent materials in the searching space are screened by the band gap which is larger than 2.8 eV to be transparent in visible range. It should be noted that some transparent materials might be excluded due to the underestimation of the simulated values of band gap.[8] The 70 materials, which meet the criterion of band gap and have all necessary descriptor for ITR prediction, form accordingly more than 4800 possible candidate interfaces. In order to make the experimental validation simpler, one of the materials was fixed as SiO_2, due to its availability of synthesis and low thermal conductivity. Several transparent materials were predicted with high ITR with SiO_2 as shown in Fig. 2. The Bayesian optimization of COMBO was applied to select the materials from those with higher intrinsic thermal conductivity, and after several cycles between prediction and feedback of experimental data, interface of TiO_2/SiO_2 is selected. The experimental ITR of TiO_2/SiO_2 is close the predicted values in Fig. 2.

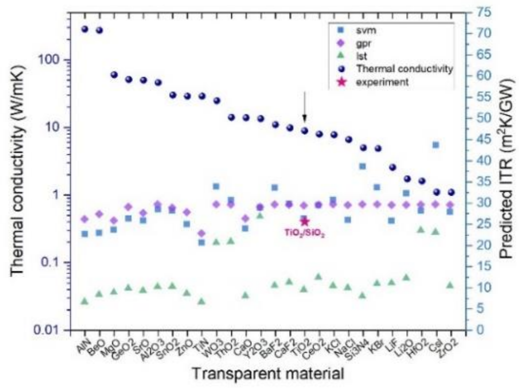

Fig. 2 The thermal conductivity and predicted ITR of transparent material candidates.

3.2 Thermal conductivity

The thermal conductivity (k) of the samples with various interface number (N) is shown in Table 2. The R_0*, which subtracted the ITR of Au/SiO_2(5 m^2K/GW)[9] from R_0, is the ITR of all interfaces of TiO_2/SiO_2. The thermal conductivity decreases from 0.26 to 0.21 W/mK of samples on Qz and from 0.96 to 0.54 W/mK of samples on Si with increasing interfaces by five times. All the samples deposited on Qz show lower thermal conductivities relative to the ones on Si substrates. As the thickness of each layer decreases, the ITR of each interface (R_0*/N) decreases. The thermal conductivity of TS-Qz-1 achieves very low thermal conductivity of 0.21 W/mK, which is even lower than the reported transparent layered materials, such as ZrO_2/Y_2O_3,[10] and Y_2O_3/SiO_2.[11]

Table 2 Thermal conductivity of samples

Sample	***N***	***k* (W/mK)**	***R*₀*/*N***
TS-Qz-30	2	0.65	25.64
TS-Qz-5	20	0.26	15.71
TS-Qz-1	100	0.21	4.08
TS-Si-30	2	0.97	10.38
TS-Si-5	20	0.96	1.82
TS-Si-1	100	0.54	1.18

3.3 Substrate dependence

The XRD of the TiO_2/SiO_2 samples is shown in Fig. 3. The phases both show in the samples on Qz and Si substrates are rutile TiO_2(210) and Au of the top layer, indicating that the films are composed of crystalline TiO_2 and amorphous SiO_2. The peak of SiO_2(100) comes from the substrate of Qz instead of the layered thin film. Interestingly, we found the additional phases of Ti_2O_3 (104) (110) and (214) exist in the samples on Si substrates, even as the samples with the same thickness of each layer on Qz and Si were deposited simultaneously in the same sputtering. These additional phases may be attributed to the same atomic environment (tetrahedron) of O in Ti_2O_3 and Si and the similar atomic distance between O-Ti (0.203 nm) and Si-Si (0.235 nm). Besides, the peak intensity of Ti_2O_3 (104) increases with the increasing interface numbers, implying the strong relation between Ti_2O_3 phase and interfacial region.

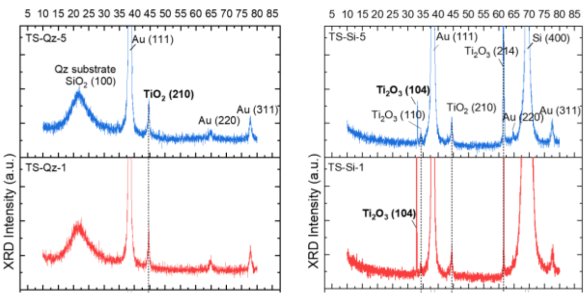

Fig. 3 XRD of TiO_2/SiO_2 on Qz (left) and Si (right) substrates.

4. Summary

The extrapolative search by adaptive learning is applied combining with the previous proposed ITR model to search potential materials for transparent thermal insulators. The selected material system of SiO_2/TiO_2, nanoscale-layered thin films synthesized by sputtering, show ultra-low thermal conductivity of 0.21 W/mK and high transparency (>90%). The thermal conductivity of the TiO_2/SiO_2 multilayer was reduced by 85% from SiO_2 values and attributed to the high ITR between alternating layers and low intrinsic thermal conductivity of component materials.

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