Thermal resistant efficiency of Nb-doped TiO2 thin film based glass window	Hiệu quả kháng nhiệt của màng mỏng TiO2 trên cửa sổ thủy tinh OK
Abstract. The proportional	Tóm tắt Mối liên hệ giữa hệ số

relationship between the infrared (IR) transmittance of a transparent material and its IR-induced heat transfer can be explained via a simple model. The agreement between theory and the experimental work was examined by measuring rising temperature inside a glass-window heat-insulator box under IR irradiation, where the material of the glass window was modified from corning glass (CG) to 9 at% Nb-doped TiO_2 (TNO) fabricated by sputtering deposition. The fabricated TNO thin film was mostly transparent in visible region and had low transparency in IR region, which produced the self-cooling effect inside the insulator box. In comparison to the window glass made by CG, the temperature increased inside the box would be 24% less if the window was made by TNO on CG, which is potentially applicable in manufacturing of products that have the element of energy-cut cooling. This energy-cut declines proportionally to the decrease of the glass window area.

Introduction: Increasing world energy consumption causes the rise of atmospheric CO_2 level, which is one of the main causes of global warming. Therefore, this has become a challenging subject. The transparent conductors (TCs) - oxides as well as non-oxides - can play an

truyền qua hồng ngoại (IR) của vật liệu trong suốt và khả năng truyền nhiệt cảm ứng IR có thể giải thích thông qua mô hình đơn giản. Để đánh giá sự phù hợp giữa lý thuyết và các công trình thực nghiệm, chúng tôi tiến hành đo nhiệt phát sinh bên trong một hộp cách nhiệt cửa sổ thủy tinh là thủy tinh corning (CG) được phủ bằng TiO_2 pha tạp Nb 9 at% (TNO) thông qua phương pháp phún xạ. Màng mỏng TNO chế tạo được hầu như trong suốt trong vùng khả kiến, tạo ra hiệu ứng tự làm mát bên trong hộp cách nhiệt. So với cửa sổ thủy tinh chế tạo từ CG, độ tăng nhiệt độ bên trong hộp ít hơn 24% nếu cửa sổ làm bằng TNO trên CG, có tiềm năng ứng dụng trong việc chế tạo các sản phẩm có thành phần làm lạnh hạn chế năng lượng. Khả năng hạn chế năng lượng giảm theo sự giảm diện tích cửa sổ thủy tinh.

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important role in generating as well as saving energy [1]. TCs are of concern because of several reasons. Firstly, they are transparent in visible light range and absorb ultraviolet (UV) light due to excitations across an energy gap. In addition, they reflect IR radiation for wavelengths longer than the plasma wavelength [2].	[redacted]
IR-reflective properties of TCs have been reported before, such as Sn-doped In_2O_3 (ITO) [3-7], Al-doped ZnO (AZO) [8-10], and F-doped SnO_2 (FTO) [11-13]. Nb-doped TiO_2 (TNO) is a newcomer TC [14-17]; and TiO_2 has attributes that other conventional host materials of TCs do not possess, namely the high refractiveindex [18], the large static permittivity [19], the highchemical stability especially in a reducing atmosphere [20], and the photocatalytic [21]. TNO thin films have some benefits, including its low cost, chemical stability, easy fabrication, and self-cleaning ability. As a result, they have potential value as an energy-saving coating layer for "cool" window glass, which aims to minimize temperature rise of	[redacted]

black interior household appliances caused by IR-light absorption from solar irradiation [22,23].	[redacted]
A well-known model of solar-reflective "cool" coatings was introduced by Levinson *et al.* with a full complication of the relationship between the backscattering, absorption coefficient of the coating material and the solar irradiation spectrum [24]. This model was well applicable to different colored "cool" coating pigments [25-27]. Later, Jitka *et al.* brought out a simplified in-lab technique that targeted the evaluation of heat-induction inside a glass-window box [28]. It was widely used for different transparent IR-reflective materials [29-31]. However, given the heat conductance and outside surface temperature of the glass window, the model was still complicated. Therefore, the concrete relationship between the optical property of the material and the heat-induction inside the box had not been discussed yet.	[redacted]
In this paper, the thermal resistance effect of TNO thin film fabricated on glass window	[redacted]

was investigated. The air temperature inside a thermally insulated box was measured. The front side of the box had a small window with a glass sample. Furthermore, the effect of the area of the glass window with a temperature rise inside the box was evaluated. The theorical relationship between transmission and temperature increase was also discussed. By using TNO coated glass, the energy for cooling was calculated to decrease by 24%.	[redacted]
Experiment and methods	[redacted]
TNO thin film fabrication : TNO (Nb 9 at%) films were sputtered-deposited on unheated corning glass (CG) substrates. The sputtering process was carried out under a total pressure of 7.5×10^{-3} Torr in pure Ar atmosphere. The RF sputtering power applied to the target was kept constant at 90 W during the process. The as-deposited amorphous films were annealed at 350^{o}C in vacuum atmosphere ($\sim1\times10^{-5}$ Torr) within 30 minutes. The thickness of TNO films was determined by the cross-section scanning electron microscope (SEM) (NOVA NANOSEM) measurement. Light absorption was observed	[redacted]

by two tools, including the Shimadzu 2450 at UV-visible region from 200 nm to 900 nm, and the Shimadzu UV 3600 at near infrared (NIR) region from 800 nm to 2600 nm. The structure of the thin films was examined using a BRUKER 5005 X-ray diffraction (XRD) analyzer.

Installation of heat resistant measurement: The temperature increase in a closed box was generated by the irradiation from an IR lamp (Medilamp 250 W, TNE Co., Vietnam) (Fig.1). The box had cubic structure covered by heat-resistant Styrofoam, whose S_0 side area was 49 cm^2. A window was installed at the side to ensure that the IR rays went through. The S area of the window could be modified. Inside the box, the black foam was fixed in order to create maximum IR absorption. The IR lamp was placed in front of the window within the same distance in all measurements. The IR power that irradiated to the window and the box could be considered constant. The room temperature and the temperature in the box (T) were measured by a digital thermometer (Conotec,

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Korea) at different timings after the lamp had been turned on, respectively at 1, 2, 3, 5, 7, 10, 15, 20 and 30 min. The measurement was carried out as the area of the window varied between 4, 9, 16 and 25 cm^2. At each size, the process was repeated within 3 different days to check reproducibility. During the experiments, "active cooling" of the window surface was employed by an air ventilator. **Results and discussion** With similar fabrication conditions, the thickness and XRD pattern of the TNO thin film were the same as our other TNO thin film product [32] (Fig.2). The thickness of the film was about 230 nm. In comparison to the characteristics of standard anatase TiO_2 (JCPDS No. 021-1272), all the detected XRD peak positions of our sample slightly shifted to smaller angles. This transition corresponded with the larger length of the a- and c-axes of the unit cell, which was originated from the bigger radius size of Nb^{5+} ion compared to Ti^{4+} ions and resonated with Vegard's law [14,17]. Besides, no impurity of Nb_2O_5 was detected, as we were	[redacted] [redacted] [redacted]

able to observe that Nb^{5+} ions were fully doped to TiO_2 lattice.	[redacted]
The transmittance spectra of the CG sample and TNO thin film on CG sample are shown in Fig. 3. In the whole range from 400 nm to 2600 nm containing UV-vis and IR regions, corning glass transfers more than 90% of light. Regardless of the presence of doped Nb^{5+} ions, our TNO thin film is observed to have high carrier concentration, which is estimated to be 8×10^{21} cm^{-3} by Hall measurement (data not shown). This generates plasmonic reflectivity at IR region [14-17]. As a result, the transmittance spectrum of our TNO thin film at IR region is as low as 70%. Besides, a wave-like spectrum is detected in the UV-vis region of 400 nm to 1000 nm, which might correspond with the light interference on the thin film.	[redacted]
Mean near-IR transmittance was calculated by the formula $T_{IR} = \frac{\sum_{2600nm}^{800nm} Abs_i \times \lambda_i}{\sum_{\lambda_1}^{\lambda_2} \lambda_i}$,	[redacted]
where T_i is transmittance at λ_i	

wavelength. Through this formula, the mean near-IR transmittance of CG and TNO on CG are respectively T_{IR}^{CG} = 92.1 % and T_{IR}^{TNO} = 72.7%. If the all IR irradiation in this range is totally absorbed by the black foam inside the box (Fig.1) and is fully transferred to produce heat, the temperature increase inside the box will depend on the window materials proportional to the mean near-IR transmittance values.

The differential equation of the temperature inside the box could be written as following:

$$k_1 SP + k_2 (S_0 - S) P + (T$$

(1)

P is heat flux of the IR resource; S and S_0 are respectively the area of the window and of irradiated side of the box. S_B is the total area of the box - in our case, the box is cubic, hence $S_B = 6S_0$. The heat transfer efficiencies, which mean the heat percentage that increases the temperature of the internal part of the box, are k_1 relating to the window material and k_2 as the box material. As the temperature of the internal part of the box rises, the heat starts releasing. This release is

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proportional to the temperature difference between the internal part of the box (T) and the room (T_0). The heat release efficiencies are labeled as σ_1 and σ_2 relating to the window and the box, respectively.	[redacted]
Two new values are defined, $\frac{\wp(S)}{C}=\frac{k_1SP+k_2(S_0-S)P}{C}$, $\frac{\sigma(S)}{C}=\frac{\sigma_1S+\sigma_2(S_B-S)}{C}$, which are later defined as heat transfer rates regarding the heat induction and heat release processes. The differential equation could be simplified as below:	[redacted]
$$\frac{\wp(S)}{C}+\frac{\sigma(S)}{C}(T-T_0)=$$ (2)	
The solution of the first order differential equation is an exponential time-dependence, which would be $T=T_1+T_2e^{-kt}$. Applying this to the equation (2), we result in the following calculation:	[redacted]
$$T(S,t)-T_0=\frac{\wp(S)}{\sigma(S)}-\frac{\wp(}{\sigma(}$$ (3)	
The temperature increase inside the box exponentially	

depends on the irradiation time and the area of the window. Fig. 4 and Fig. 5 respectively show the time dependence of temperature increase inside the box with different glass window areas based on CG and TNO on CG. All the experiments were repeated 3 times on different days and the high reproducibility was achieved with the mean standard error of the temperature increase smaller than 2%.

As visualized in Fig. 4 and Fig. 5, the temperature increase is exponentially dependent on time, which resonates well with the equation (3). By fitting the experimental data into the exponential function showed in (3) using the Gnuplot program, the $\frac{\wp(S)}{\sigma(S)}$ and $\frac{\sigma(S)}{C}$ values can be estimated. From those, $\frac{\wp(S)}{C}$, $\frac{\sigma(S)}{C}$ heat transfer rates are calculated and showed in Fig. 6. These heat transfer rates are linearly dependent on the window area, which agrees well with our model mentioned in equation (1). Rewrite the definitions:

$$\frac{\wp(S)}{C} = \frac{k_2 P S_0}{C} + \frac{(k_1 - k_2) P S_0}{C} \left(\frac{S}{S_0} \right)$$

and

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$$\frac{\sigma(S)}{C} = \frac{\sigma_2 PS_0}{C} + \frac{(\sigma_1 - \sigma_2)PS_0}{C}\left(\frac{S}{S_0}\right) .$$

Once, linear fitting is used to calculate the *S*-depending values, from those $\frac{\wp(S)}{C}$, $\frac{\sigma(S)}{C}$ values are considered at boundary conditions – $S = 0$ as the box being constructed without glass window and $S = S_0$ as the glass window fitting the full size of one box-side.

Table 1 indicates the calculated $\frac{\wp(S)}{C}$, $\frac{\sigma(S)}{C}$ heat transfer rates with full size windows made from CG and TNO on CG. At $S = S_0$ boundary condition, $\frac{\wp(S = S_0)}{C} = \frac{PS_0}{C} k_1$ equals to 6.97 ± 0.53 ${}^{o}C/\min$ for CG window and 5.39 ± 0.53 ${}^{o}C/\min$ for TNO on CG window. With this condition, the $\frac{\sigma(S = S_0)}{C} = \frac{PS_0}{C}(\sigma_1 + 5\sigma_2)$ rates are 0.22 ± 0.04 $\min^{-1}$ and 0.18 ± 0.04 $\min^{-1}$. By replacing these heat transfer rates to equation (3), the saturation temperature increase inside the box could be estimated and respectively equals to 33.6± 3.1 °C and 27.5 ± 2.6 °C for CG and TNO on CG window. In the other vocalization, in comparison to

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the box built with CG-window, the cooling energy is required to match the temperature inside the box with outside temperature with a 24% cut if the window is made by TNO on CG.

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The ratio of the heat transfer rates between the two windows – TNO on CG and CG – is estimated to be $\frac{\wp^{TNO}(S=S_0)}{C} \Big/ \frac{\wp^{CG}(S=S_0)}{C} = \frac{k_1^{TNO}}{k_1^{CG}} \approx$ 77.3%, which is very close to the ratio of mean IR-transmittance between two materials, $T_{IR}^{TNO} \big/ T_{IR}^{CG} = 78.9\%$. The small difference between these two values might correspond with the very low heat conduction of corning glass material, with the surface temperature of the window being passively cooled by air ventilator, and with the correlation between the IR-lamp irradiated spectrum and the IR-transmittance spectrum of the material [24]. Besides, the heat release rate $\frac{\sigma(S=S_0)}{C}$ contains two main parts: heat conduction by the material and Boltzmann radiation heat release [28], which is relatively small comparing to

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the low heat release from the box to external environment.	[redacted]
By writing $S = 0$ as boundary condition, we have $\frac{\wp(S=0)}{C} = \frac{PS_0}{C} k_2$, $\frac{\sigma(S=0)}{C} = \frac{5PS_0}{C}\sigma_2$. This means that the heat transfer rates are independent of the window material. The experiment data shows that the $\frac{\wp(S=0)}{C}$ equals to 0.77 ± 0.13 $^{o}C/_{\min}$ for CG window and 0.69 ± 0.12 $^{o}C/_{\min}$ for TNO on CG window (Table 2). These values are mostly identical in their standard error range, which agrees with our suggested model. The same result is achieved with the $\frac{\sigma(S=0)}{C}$ rate. Further, the $k_1/k_2 \approx 11$denotes that the heat transfer by the box materials is very small in comparison to the heat transfer by the window material.	[redacted] [redacted]
By setting up the experiment, we minimized the heat conduction and Boltzmann radiation between the internal space and external space of the box. As a result, the heat transfer rate related to the IR-irradiation	[redacted]

from IR-lamp is proportional to the mean IR-transmittance of the glass window material.	[redacted]
Conclusion: We have brought out a simplified model to investigate the IR-irradiation-generated temperature increase inside a glass window heat insulated box. The experimental work was carried out on two materials of glass window: CG and TNO on CG. The black foam inside the box absorbed IR-rays that went through the glass window, hence made the temperature inside the box rise. As shown in the model, this temperature increase depends on the irradiation period and heat transfer rate of the glass window. In summary, the study indicates the following points:	[redacted]
1. The IR-transmittance of the window material is proportional to the heat transfer rate from the IR-lamp to the internal space of the box.	[redacted]
2. TNO thin films sputtered on CG are good for glass window materials in smart construction targeted for “self-cooling” applications.	[redacted]
3. The model is suitable for	[redacted]

only insulator boxes with active cooling surface. Besides, the correlation between the IR-lamps and IR-transmittance of the glass window sample needs to be investigated in order to create a good match between experimental work and theories. **Acknowledgements:** This study is supported by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under project number 103.02-2014.78. The authors thanks the Center for Materials Science -, Faculty of Physics, Nano and Energy Center, Hanoi University of Science and the project named "Strengthening research and training capacity in fields of Nano-Science and Technology, and Application in Medical, Pharmaceutical, Food, Biology, Environmental protection and Climate Change adaptation in the direction of sustainable development" for providing us with relevant equipment and research facilities. We are also grateful to Dr. Thu Le from the Riken Metamaterials Laboratory for the IR spectra measurement.	[redacted] [redacted] OK