BNL-105048-2014-CP

Measuring Refractive Index Profiles within Thin-Film Photovoltaics with High Spatial Resolution using the Modified IM-IWKB Method

Yutong Pang[1,2] and Matthew D. Eisaman[1,2,3]
1Sustainable Energy Technologies Dept., Brookhaven National Laboratory, Upton, NY 11973 USA
2Department of Physics and Astronomy, Stony Brook University, Stony Brook, NY 11790 USA
3Department of Electrical & Computer Engineering, Stony Brook University, Stony Brook, NY 11790 USA

Presented at the 40th IEEE Photovoltaic Specialists Conference
Brookhaven National Laboratory, Upton, NY
June 8-13, 2014

May 2014

Sustainable Energy Technologies Department

Brookhaven National Laboratory

U.S. Department of Energy
DOE Office of Science

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE-AC02-98CH10886 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

This preprint is intended for publication in a journal or proceedings. Since changes may be made before publication, it may not be cited or reproduced without the author's permission.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Measuring Refractive Index Profiles within Thin-Film Photovoltaics with High Spatial Resolution using the Modified IM-IWKB Method

Yutong Pang[1,2] and Matthew D. Eisaman[1,2,3]

[1]Sustainable Energy Technologies Dept., Brookhaven National Laboratory, Upton, NY 11973 USA
[2]Department of Physics and Astronomy, Stony Brook University, Stony Brook, NY 11790 USA
[3]Department of Electrical & Computer Engineering, Stony Brook University, Stony Brook, NY 11790 USA

***Abstract* — We derive a correction to the phase contribution for the reconstruction of refractive index profiles within thin-film photovoltaics using the Index Matched Inverse Wentzel-Kramers-Brillouin (IM-IWKB) Method. We quantify the improvement of the refractive-index reconstruction due to this modification for structures typical of organic photovoltaics. Near the low-index surface of the photoactive layer, this modification reduces the fractional error in the reconstructed profile by a factor of ten, resulting in a highly accurate refractive index reconstruction throughout the entire film thickness. This technique is applicable to the reconstruction of the refractive index profiles within any thin-film photovoltaic material.**

***Index Terms* — photovoltaic cells, refractive index, semiconductor films, semiconductor waveguides, solar energy, thin films.**

I. Introduction

We recently introduced the Index Matched Inverse Wentzel-Kramers-Brillouin (IM-IWKB) Method as a new technique for the reconstruction of refractive index profiles (RIPs) with high spatial resolution within the photoactive layers of thin-film photovoltaics for films as thin as 200 nm [1]. The conventional IWKB method [2]-[3] is a well-known technique for reconstruction of the RIPs of various films, although this approach is only valid for relatively thick (≥ 2 μm) films for visible wavelengths, since the number of points in the reconstructed RIP is equal to the number of modes supported by the film at that wavelength. The IM-IWKB method [1] modifies the IWKB method by depositing a relatively thick (1-10 μm) index-matched, non-absorbing layer below the thin photoactive layer of interest, and then applies the IWKB method to this system, resulting in a greatly improved spatial resolution for the RIP reconstruction within the thin photoactive layer. The IM-IWKB technique results in a spatial resolution of ~10 nm (at a wavelength of 500 nm) in thin (200 nm) films, an improvement of more than a factor of ten compared to the traditional IWKB. Importantly, this improvement in spatial resolution makes the IM-IWKB method applicable to the measurement of RIPs of the absorber layers of organic photovoltaics, and other thin-film photovoltaics with absorber layer thicknesses less than 2 μm [1]. While RIPs for such thin layers can be obtained using spectroscopic ellipsometry, IM-IWKB requires no free parameters, which is a significant advantage compared to the parameterized, model-based technique used in ellipsometry. This generally allows for much higher spatial resolution using IM-IWKB compared to ellipsometry.

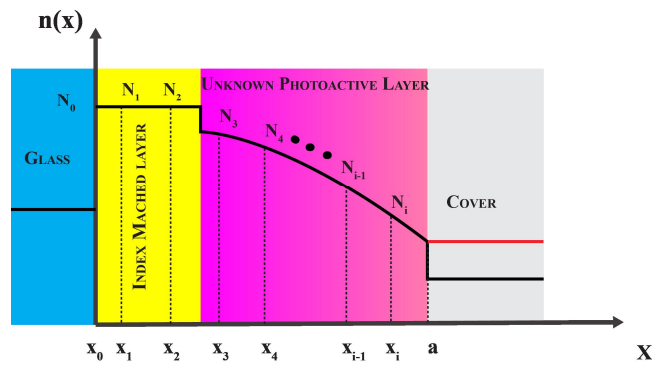

Fig. 1. Refractive index profile n(x) considered in our calculations. Red (Black) line: Index profile that is continuous (discontinuous) at x=a. (N_i, x_i) represents the (effective index, turning point) for guided mode *i*, and *a* represents the thickness of the index-matched layer + unknown photoactive layer.

Previous demonstration of both the IWKB and the IM-WKB methods assume a constant phase shift equal to π/4 at the turning point in the film. For thick films where IWKB is applicable, this approximation is justified. However, the assumption of a phase shift of π/4 becomes increasingly unjustified as the thickness of the film is decreased. In the case of thin films less than one micron in thickness, for which IM-IWKB is appropriate, this assumption results in an error in the reconstructed RIP.

In this paper, we derive a correction to this phase shift term for the case of thin films, and demonstrate the improved accuracy of IM-IWKB when using this modified phase contribution compared to the standard case of π/4. We first describe the mathematical basis of our approach, and then apply it to a computational example that assumes an RIP of a "canonical" organic photovoltaic (OPV) system to demonstrate that the method with modified phase shift achieves improved accuracy.

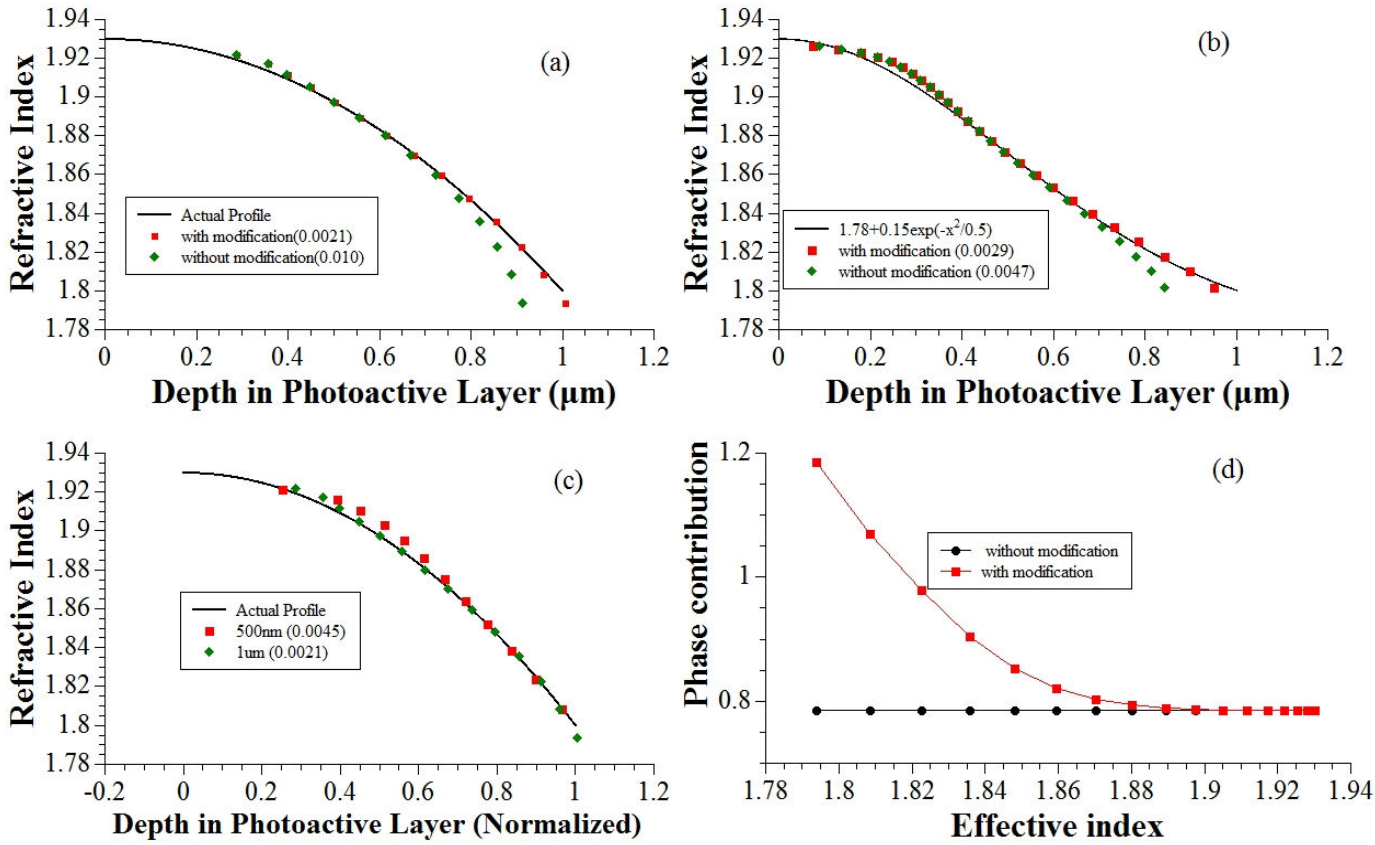

Fig. 2. Reconstructed RIPs of the photoactive layer for TE-polarized light at a wavelength of 500 nm performed by the IM-IWKB method both with and without phase modification using guided mode effective indices obtained via FDTD simulation for the structure (see Fig. 1 black line, discontinuous at x=a): substrate(semi-infinite, n=1.76)/index-matched layer (n=1.93)/photoactive layer("Actual Profile" (solid black line): $n(x)=1.93-0.13(x/t_{PA})^2$ unless otherwise stated)/cover(n=1). (t_{PA}, t_{IM}) = thickness of the (photoactive layer, index-matched layer). Number in parentheses in legend is the root mean squared difference between the reconstruction and the actual profile. (a) Substrate(semi-infinite, n=1.76)/index-matched layer(t_{IM} = 5 μm, n=1.93)/photoactive layer(t_{PA} = 1μm)/cover both with (red) and without (green) phase modification. (b) Substrate(semi-infinite, n=1.76)/index-matched layer(t_{IM}=10 μm, n=1.93)/photoactive layer(t_{PA} = 1μm, Gaussian profile)/cover both with (red) and without (green) phase modification. (c) With phase modification for two values of t_{PA} (500 nm and 1 μm) for substrate(semi-infinite, n=1.76)/index-matched layer(t_{IM} = 5 μm, n=1.93)/photoactive layer(t_{PA} =500 nm, 1 μm)/cover, with depth in photoactive layer normalized to 1. (d) Dependence of phase contribution ϕ_i on the effective index in the cases with (red square) and without (black circle) phase modification for the structure substrate(semi-infinite, n=1.76)/index-matched Layer(5 μm, n=1.93)/photoactive Layer(t_{PA} =500 nm)/cover.

II. METHODOLOGY

Consider a multi-layer thin-film stack with a monotonically decreasing RIP, consisting of glass substrate, index-matched layer with known, constant refractive index, photoactive layer with unknown RIP, and cover as shown in Fig. 1. (N_i, x_i) represents the (effective index, turning point) for guided mode *i*, and *a* represents the thickness of the index-matched layer + unknown photoactive layer. As shown in recent work on the IM-IWKB method [1], by applying the IWKB method to this system with a 1-10μm thick index-matched layer, the unknown RIP of a 200 nm thick P3HT:PCBM photoactive layer can be reconstructed with an average spatial resolution of about 20 nm by measuring the guided-mode effective indices (N_i) of the multi-layer stack at a wavelength of 829 nm, with a 430 μm thick sapphire substrate replacing the glass layer shown in Fig. 1, and a 5 μm thick AlN film used for the index-matched layer. This same work also demonstrated the ability of the IM-IWKB method to measure the evolution of the phase segregation within the P3HT:PCBM bulk heterojunction film during annealing by calculating the spatial profile of the P3HT and PCBM volume fractions from the measured RIP via application of the effective medium approximation [1].

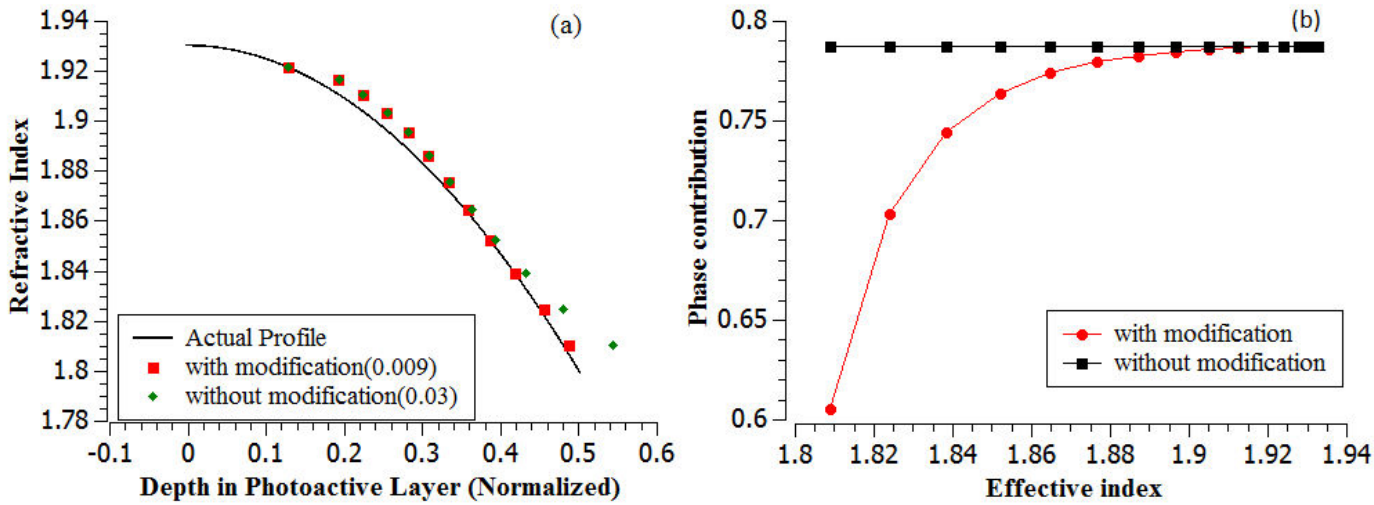

Fig. 3. Reconstructed RIPs of the photoactive layer for TE-polarized light at a wavelength of 500 nm performed by the IM-IWKB method both with and without phase modification using guided mode effective indices obtained via FDTD simulation for the structure (see Fig. 1 red line, continuous at x=a): substrate(semi-infinite, n=1.76)/index-matched layer (n=1.93)/photoactive layer("Actual Profile" (solid black line): $n(x)=1.93-0.13(x/t_{PA})^2$ unless otherwise stated)/cover. (t_{PA}, t_{IM}) = thickness of the (photoactive layer, index-matched layer). Number in parentheses in legend is the root mean squared difference between the reconstruction and the actual profile. (a) Substrate(semi-infinite, n=1.76)/index-matched layer(t_{IM} = 5 μm, n=1.93)/photoactive layer(t_{PA} = 0.5μm)/cover(n=1.8) both with (red square) and without (green diamond) phase modification. (b) Dependence of phase contribution ϕ_i on the effective index in the cases with (red circle) and without (black square) phase modification for the structure substrate(semi-infinite, n=1.76)/index-matched Layer(5 μm, n=1.93)/photoactive Layer(t_{PA} =500 nm)/cover(n=1.8).

The IM-IWKB method reconstructs the RIP from the measured N_i by the recursive solution of the IWKB characteristic equation:

$$x_i = \frac{(i-1)\pi + \phi_0(N_i) + \phi_i - \sum_{j=1}^{i-1} k\{x_j[(N_{avg,j}^2 - N_i^2)^{\frac{1}{2}} - (N_{avg,j+1}^2 - N_i^2)^{\frac{1}{2}}]\}}{k(N_{avg,i}^2 - N_i^2)^{\frac{1}{2}}}, \quad i = 1,2,3 \tag{1}$$

where $N_{avg,i} = (N_i + N_{i-1})/2$, relies on backward averaging of the effective indices to obtain values between the measured ones, and $k = 2\pi/\lambda$ is the free-space wavenumber. The quantity ϕ_i in (1) represents the phase contribution from the turning point x_i. The phase contribution ϕ_i is typically assumed to be a constant value of $\pi/4$ [4], which is a good approximation for the thick-film case. However, for the case of thin films (< 1μm thick) relevant to the IM-IWKB method and many thin-film photovoltaics, ϕ_i must be modified, especially for modes that have turning points near the cover interface [5].

In this paper, to demonstrate the improved accuracy of IM-IWKB when using this modified phase shift term, the thin-film structure is divided to two cases. The first example is the structure shown in Fig. 1 (black line), where the index profile is discontinuous at x=a. For this case, the phase contribution ϕ_i is given by (2). The second example is the structure shown in Fig. 2 (red line), where the index profile continuous at x=a, in which case the phase contribution ϕ_i is given by (3):

$$\phi_i = \tan^{-1}\left\{\frac{r_0 P_{a^+}[\mathrm{Bi}(\xi_1) + \mathrm{Ai}(\xi_1)] + \mathrm{D}_1^{1/3}[\mathrm{B}_i'(\xi_1) + \mathrm{A}_i'(\xi_1)]}{r_0 P_{a^+}[\mathrm{Bi}(\xi_1) - \mathrm{Ai}(\xi_1)] + \mathrm{D}_1^{1/3}[\mathrm{B}_i'(\xi_1) - \mathrm{A}_i'(\xi_1)]}\right\} \tag{2}$$

$$\phi_i = \frac{\pi}{4} + \tan^{-1}\left[\frac{P_{a^+} A_i(\xi_2) - \mathrm{D}_2^{1/3} A_i'(\xi_2)}{P_{a^+} B_i(\xi_2) - \mathrm{D}_2^{1/3} B_i'(\xi_2)}\right], \tag{3}$$

where $r_0 = 1$ for TE modes, $r_0 = n^2(a^-)/n^2(a^+)$ for TM modes, $Ai(x)$ and $Bi(x)$ are Airy functions, and for convenience we define:

$$P^2 = k^2(N_i^2 - n^2(x)) \tag{4}$$

$$P_{a^+} = P(x = a^+) \tag{5}$$

$$P_{a^-} = P(x = a^-) \tag{6}$$

$$D_1 = k^2[N_i^2 - n^2(x = a^-)]/(a - x_i) \tag{7}$$

$$D_2 = k^2[n^2(x = a^-) - N_i^2]/(a - x_i) \tag{8}$$

$$\xi_1 = \xi(x = a^-) = P_{a^-}^2 D_1^{-2/3} \tag{9}$$

$$\xi_2 = \xi(x = a^+) = P_{a^+}^2 D_2^{-2/3} \tag{10}$$

Now that we have derived a modified expression for the phase contribution ϕ_i, we can apply this modified IM-IWKB technique to the reconstruction of RIPs typical for P3HT:PCBM bulk heterojunction absorber layers in organic photovoltaics [1]. The RIP is reconstructed via modified IM-IWKB by the following iterative method:

(1) Use IM- IWKB method ($\phi_i = \pi/4$) to determine the initial set of x_i.
(2) Use the initial set of x_i and corresponding N_i to calculate the modified phase contribution ϕ_i
(3) Use the modified phase contribution ϕ_i to calculate a new set of x_i'. Calculate difference δ between the initial x_i and the modified x_i': $\delta = |x_i' - x_i|$.
(4) Repeat steps (2) and (3) until δ for successive sets of x_i is sufficiently close to zero.

In order to perform step (2), we need to know the thickness *a*, which can be obtained with the following approximation:

$$a = x_{i=f} + (x_{i=f} - x_{i=f-1})/2 \qquad (11)$$

Where $x_{i=f}$ is the last mode with an effective index larger than the unknown photoactive layer refractive index at the cover interface (x=a). This requires knowledge of the minimum refractive index values in the film of interest, which can be obtained by using a surface-plasmon-mode resonance measurement [6].

To quantify the improvement due to the modified phase contribution, we use Finite-Difference Time-Domain (FDTD) calculations to construct a sample structure with a known RIP and solve for the effective indices of the guided modes. These effective index values are then used to reconstruct the RIP using the IM-IWKB method both with $\phi_i = \pi/4$, and with the modified phase contribution. We compare the accuracy of the reconstruction with and without the phase-shift correction.

III. NUMERICAL RESULTS AND DISCUSSION

The results of this comparison are shown in Fig. 2 and 3, which show the reconstructed RIPs performed by the IM-IWKB method using guided mode effective indices obtained via FDTD simulation for the two cases shown in Fig. 1 – continuous (red line) and discontinuous (black line) refractive-index profile at x=a. We first consider the case where the refractive profile is discontinuous at x=a (black line in Fig. 1). From Fig. 2(a) and 2(b), we see significant improvement in the agreement between the reconstruction and the actual profile when the modified phase term is used, especially for points near the interface between the photoactive layer and the cover. Averaged over the entire thickness of the photoactive layer, modifying the phase contribution reduces the root mean squared difference between the reconstruction and the actual profile from 0.01 to 0.002 in Fig. 2(a) and from 0.005 to 0.003 in Fig. 2(b). Fig. 2(c) shows that the modified IM-IWKB maintains this improved accuracy near the cover interface (x=a) even for films as thin as 500nm. Finally, Fig. 2(d) shows calculated value of ϕ_i as a function of the effective index of the mode for the structure: substrate(semi-infinite, n=1.76)/index-matched Layer(5 μm, n=1.93)/photoactive Layer(t_{PA} =500 nm)/cover(n=1). We see that modified phase ϕ_i (red squares) increasingly deviates from $\pi/4$ (black circles) as the effective index decreases. This makes physical sense as these lower-index modes are less strongly confined and have turning points near the interface of the photoactive layer and cover, and are therefore more strongly affected by the index/index-slope discontinuity at this interface.

In Fig. 3, we consider the case where the refractive profile is continuous at x=a (red line in Fig. 1). Fig. 3(a) shows that by introducing the modified phase contribution, we can increase the accuracy of the reconstruction, especially for modes whose turning points are near the cover interface (x=a). Fig. 3(b) shows calculated value of ϕ_i as a function of the effective index of the mode for the structure: substrate(semi-infinite, n=1.76)/index-matched Layer(5 μm, n=1.93)/photoactive Layer(t_{PA} =500 nm)/cover(n=1.8). We see that modified phase ϕ_i (red squares) increasingly deviates from $\pi/4$ (black circles) as the effective index decreases. As in the discontinuous case, this makes physical sense as these lower-index modes are less strongly confined and have turning points near the interface of the photoactive layer and cover, and are therefore more strongly affected by the index-slope discontinuity at this interface. This is also consistent with Fig. 2(a), 2(b) and Fig. 3(a), which show the most dramatic improvement at the cover interface. The modified phase term ϕ_i for the continuous case is always less than $\pi/4$ (see Fig. 3(b)), whereas in the discontinuous case where the modified phase term is always greater than $\pi/4$ (see Fig. 2(d)), as can be understood by inspecting Eqs. (2) and (3).

In summary, we have developed a modified phase contribution for the IM-IWKB method [1] for the reconstruction of refractive-index profiles within thin-film photovoltaic absorber layers, and quantified the improvement due to this modification for structures typical of organic photovoltaics. Near the low-index surface of the photoactive layer, this modification improves the error in the reconstructed profile from about 2% for unmodified IM-IWKB to less than 0.2% for modified IM-IWKB. Future work will apply this technique to the in situ measurement of phase segregation evolution during the annealing of bulk heterojunction organic photovoltaics. Although we focused on the application of this technique to organic photovoltaics, this technique is applicable to the reconstruction of the refractive-index profile within any thin-film photovoltaic material.

ACKNOWLEDGEMENT

This work was partially supported by the U.S. Department of Energy, Sustainable Energy Technologies Department under Contract DE-AC02-98CH10886, and by the Laboratory

Directed Research and Development Program at Brookhaven National Laboratory.

REFERENCES

[1] Y. T. Pang, M. Bossart, and M. D. Eisaman, "Index-matched IWKB method for the measurement of spatially varying refractive index profiles within thin-film photovoltaics," *Optics Express*, vol. 22, issue S1, pp. A188-A197, 2014.

[2] K. S. Chiang, "Construction of refractive-index profiles of planar dielectric waveguides from the distribution of effective indexes," *J. Lightwave Technol.*, vol. 3, pp. 385-391, 1985.

[3] L. P. Shi, E. Y. B. Pun, and P. S. Chung, "Extended IWKB method for determination of the refractive index profile in optical waveguides," *Optics Letters*, vol. 20, pp. 1622-1624, 1995.

[4] Z. Cao, Y. Jiang, Q. Shen, X. Dou, and Y. Chen, "Exact analytical method for planar optical waveguides with arbitrary index profile," *J. Opt. Soc. Am. A*, vol. 16, pp. 2209-2212, 1999.

[5] X. Feng and Y. Gar Lam, "A modified WKB method for the improved phase shift at a turning point," *J. Lightwave Technology,* vol. 12, pp. 443-452, 1994.

[6] Tang, Y., X. Zeng, and J. Liang, "Surface Plasmon Resonance: An Introduction to a Surface Spectroscopy Technique," Journal of Chemical Education, vol. 87, pp. 742-746, 2010.