Glucose concentration sensor based on enhanced surface plasmon resonance by ITO film using Au nanowires array and ZnO-graphene hybrid nano-sheet

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A wide range glucose concentration detection method based on surface plasmon resonance in near infrared wave is proposed. A novel prism coupling structure is designed for glucose concentration sensor, and the indium tin oxide(ITO) film and ZnO-graphene hybrid nano-sheet is chosen to enhance surface plasmon resonance based on Au nanowires array. The thickness of each dielectric layer for the structure designed are analyzed to get the optimal value by finite element method, in order that the sensitivity of glucose concentration sensor is able to be enhanced greatly. The optimal thickness of each dielectric layer are given, and the sensitivity of surface plasmon resonance glucose concentration sensor can reach as high as 0.0395º/(g/L) conc. in the wide detection range of glucose concentration, 0g/L～100g/L conc. And the relationship between glucose concentration and surface plasmon resonance angle are obtained in the detection range of glucose concentration.

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1. Introduction

The test and detection devices based on surface plasmon resonance (SPR) have been paid more and more attention and have become a research hotspot[1-3]. The continuous, rapid and security detection of glucose concentration is an important technology in the biomedical field, and also is an important research direction in the biomedical field. For the detection of glucose concentration, there are some conventional and mature detection methods such as fluorescence method[4], glucose oxidase method[5], electrochemical method[6], laser roman spectrum[7] and fiber-optic method[8]. However, there is no research on wide range and high sensitivity glucose concentration detection by means of SPR so far, which could be helpful to develop a new optical detection device for glucose concentration detection. Thus, a novel structure based on SPR is designed to make a new glucose concentration sensor in this paper, which has the ability of glucose concentration detection and has features of higher sensitivity, higher accuracy, wider range and easy operation, compared with the conventional sensor and detection method.

SPR is the phenomenon that the free electron in metal surface on the interface will be caused to resonate, while the total internal reflection phenomenon exist on the interface between two mediums of metal-dielectric with different refractive index, as the incident light penetrates through the interface[9,10]. The reflection decreased greatly at a certain angle as surface plasmon resonance occurs and the corresponding angle is called SPR angle[11,12]. However the SPR angle changes correspondingly, as the refractive index of the sensing medium close to the metal surface varies. And this implies that the change in SPR angle could be determined by physicochemical properties of the sensing medium. It is found that by the study in this paper, the SPR angle changes with glucose concentration(sensing medium) because of the change in the refractive index changing with glucose concentration, and the relationship between the SPR angle and glucose concentration is given, which could provide a further theoretical preparation for making glucose concentration SPR detecting device in the future.

2. Theory and structure design

The surface plasmon resonance is very sensitive to the refractive index variation in sensing medium layer. And the refractive index of the glucose solution layer is caused to change by the glucose concentration and increase with the increasing of the glucose concentration. The relationship between glucose concentration and corresponding refractive index are shown as Fig. 1[13].

In this paper, there are various nanomaterial considering to be added into the structure while it is designed, in order to furthest enhance the sensitivity of glucose concentration SPR sensor. Metal nanowires arrays systems has a strong ability of absorbing incident light at specific frequencies of SPR[14-18]. Compared to conventional SPR sensor based on metal nano-film, an optimal metal nanowire structure can provide a greatly sensitivity enhancement (eg. by 3.44 times[19]). However, Au nanowires arrays have a good optical extinction properties[20]. Thus, Au nanowires arrays are chosen to enhance the sensitivity of SPR sensor designed in this paper.

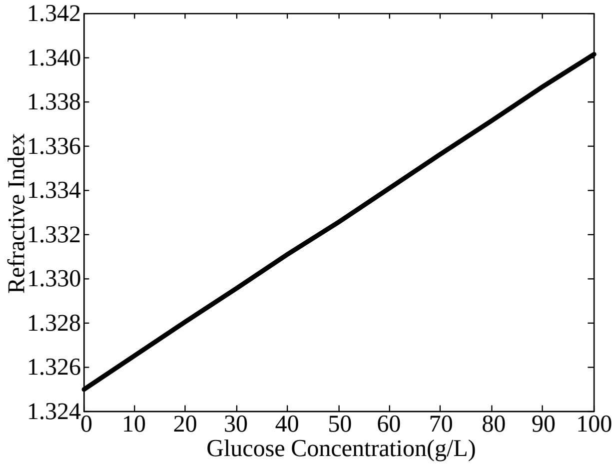

Fig. 1. Relationship between glucose concentration and refractive index

Two-dimensional nanomaterials have an extremely strong absorption properties, and are very suitable for the adsorption of adsorbate materials because of their large surface-to-volume ratio and highly conductive nature[21]. Indium tin oxide(ITO) film is a transparent oxide semiconductor that has wide gap[22], and has a good support for surface plasmon resonance wave(SPW) at the ITO-dielectric interface[23]. Thus, ITO is chosen to enhance the sensitivity of glucose concentration SPR sensor.

Graphene has high absorption coefficient from UV to far IR light(~2.3%)[24,25], the charge carrier mobility of graphene can reach as high as 106 cm2V−1s−1[26], and graphene can be used to enhance SPR. ZnO-graphene hybrid nano-sheet is also chosen to enhance the sensitivity of glucose concentration SPR sensor, because there exists wide energy band and high exciton binding energy for Zn oxide (ZnO)[27-30]. ZnO is a wide band gap semiconductor(3.37eV) and has a high exciton binding energy[31], which has an important influence on optical absorption. And the composite layer of ZnO attachment to graphene can work better than the individual graphene for SPR enhancement.

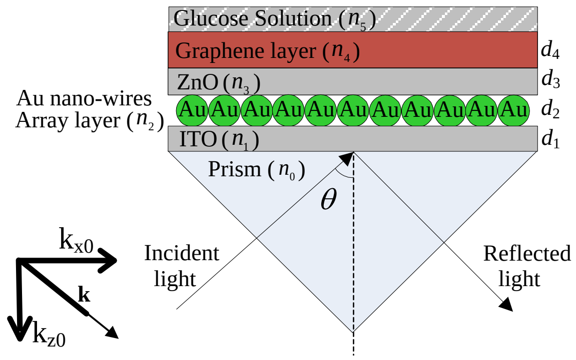

Fig. 2. Structure designed for the glucose concentration sensor (color online)

A novel prism coupling structure was designed for the glucose concentration sensor, which is composed of polymer prism, ITO, Au, ZnO-Graphene and the sample medium layer successively, as shown in Fig. 2. The polymer prism is the micro-prism made of polymer materials, the refractive index(n_0) is 1.4. For the two materials, ITO and Au, the dielectric constant is given by Drude Lorentz model:

$$\varepsilon_{\omega}(\lambda)=\varepsilon_{mr}+i\varepsilon_{mi}=1-\frac{\lambda^2\lambda_c}{\lambda_p^2(\lambda_c+i\lambda)} \tag{1}$$

Where λ_p and λ_c denote the plasma wavelength and the collision wavelengths respectively, For ITO, the values of the plasma wavelength and the collision wavelength are used: λ_p=5.6497×10^{-7}m and λ_c=11.21067×10^{-6}m[32], and For Au, the values of the plasma wavelength and the collision wavelength are used: λ_p=1.6826 × 10^{-7} m and λ_c=8.9342×10^{-6}m[33]. And the refractive index of ITO (n_1) and Au(n_2) are 0.0819+1.2362i and 0.2725+5.2342i respectively. The refractive index of ZnO (n_3)is 1.96[34]. The refractive index of graphene (n_4) is 2+0.56i[35], the monolayer thickness of which is 0.34nm, and the multilayer thickness is L×0.34nm (L is the layer number). The sample medium layer is glucose resolution, its refractive index depends on the glucose concentration. The wavelength is chosen of near infrared wave (900nm) for the incident light, to analyze and research in theory and experiment.

The finite element method is used for theoretical analysis. The finite element method is to divide the computational domain into finite elements. In each element, the differential equation is solved in discrete form by means of the variational principle, so as to obtain the solution of electromagnetic problems. The incident light, p-polarized light, falls on the metal layers through the prism by the total reflection. There exists an evanescent wave whose amplitude is decayed exponentially normal to the interface by the total reflection. When $k_{x0} = \mathrm{Re}(k_{sp})$, surface plasmon, at the interface of the metal and dielectric, are excited by the evanescent wave. The relationship between them are given as follows:

$$\varepsilon_j = n_j^2 \tag{2}$$

$$k_{sp} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_j \varepsilon_{j+1}}{\varepsilon_j + \varepsilon_{j+1}}} \tag{3}$$

$$k_{x0} = \sqrt{\varepsilon_0}\,\frac{\omega}{c}\sin\theta \tag{4}$$

where, k_{x0} is the wave number vector of the incident light across the medium, k_{sp} is the wave number vector of the surface plasmon wave, ε_j (j=0,1,2,3,4,5) is the dielectric constants of each medium layer including the prism, Au, MoS_2, GO, and the sensing medium layer respectively. n_j (j=0,1,2,3,4,5) is the refractive index correspondingly, c is the speed of light in vacuum, and ω is the frequency and θ is the angle of incidence.

When the incident light is p-polarized light, the reflection coefficient R can be given, according to the Fresnel equation and the reflectivity equation, as follows:

$$R = |r_{04}|^2 = \left|\frac{r_{01} + r_{14}\exp(2\mathrm{i}\,k_{z1}d_1)}{1 + r_{01}r_{14}\exp(2\mathrm{i}\,k_{z1}d_1)}\right|^2 \tag{5}$$

where, $r_{pq} = \dfrac{n_p^2 k_{zq} - n_q^2 k_{zp}}{n_p^2 k_{zq} + n_q^2 k_{zp}}$ is the reflection ratio of the strength for the electric field at the interface between the two adjacent medium, and $k_{zj} = \sqrt{\left(\dfrac{\omega}{c}\right)^2 n_j^2 - k_{x0}^2}$, (p=0,1,2,3,4. q=1,2,3,4,5. j=0,1,2,3,4,5).

3. Results and discussion

The optimum thickness are 2nm, 40nm, 3nm, and 2×0.34nm for ITO, Au, ZnO and Graphene respectively, which are obtained by changing one dielectric layer thickness while other dielectric layer thickness fixed.

The SPR spectrum for different layer number of Graphene, L = 1, 2 and 3, are shown as Fig. 3(a), where the thickness are 2nm, 40 nm and 3nm for ITO, Au and ZnO respectively. The solid line spectrum stands for n= 1.324 and the dash line spectrum stands for n=1.342 for the refractive index of sensing medium. It is found that from Fig.3(a), the SPR peak spectrum is not good for the two limit refractive index as L=1 and L=3, only when L=2, the SPR peak spectrum is both good for the two limit refractive index. And it is also found that, the double-layer Graphene is also optimum and suitable for other thickness of all the other layer medium by study using the finite element method.

The SPR spectrum for different thickness of Au layer, d_{Au} = 35nm, 40nm, and 45nm are shown as Fig. 3(b), where the thickness are 2nm, 3nm and 2×0.34nm for ITO, ZnO and Graphene respectively. The solid line spectrum stands for n= 1.324 and the dash line spectrum stands for n=1.342 for the refractive index of sensing medium. It is found that from Fig. 3(b), the SPR peak spectrum is not good for the two limit refractive index as d_{Au} = 35nm and d_{Au} = 45nm, only when d_{Au} = 40nm, the SPR peak spectrum is both good for the two limit refractive index. And it is also found that, the 40nm, thickness of Au layer, is also optimum and suitable for other thickness of all the other layer medium by study using the finite element method.

The effects of thickness of ITO layer on SPR angle, for the two different glucose concentration, c =0g/L and c =100g/L, are shown as Fig. 4(a), where the thickness are 40nm, 3nm, 2×0.34nm for Au, ZnO, Graphene respectively. It is viewed that, the SPR angle move towards the large angle both for c =0g/L and c =100g/L, that is, the SPR angle increases both for c =100g/L and c =0g/L, with the thickness of ITO layer increasing. However, the SPR angle increases more for c =100g/L than that for 0g/L, as the thickness of ITO layer increase. Thus, the sensitivity is enhanced when the thickness of

ITO layer increase, but there is a better SPR peak at 2nm than that at other three thickness both for the two concentration limit. And it is obtained that the optimum thickness of ITO layer is 2nm based on the enhancement of sensitivity.

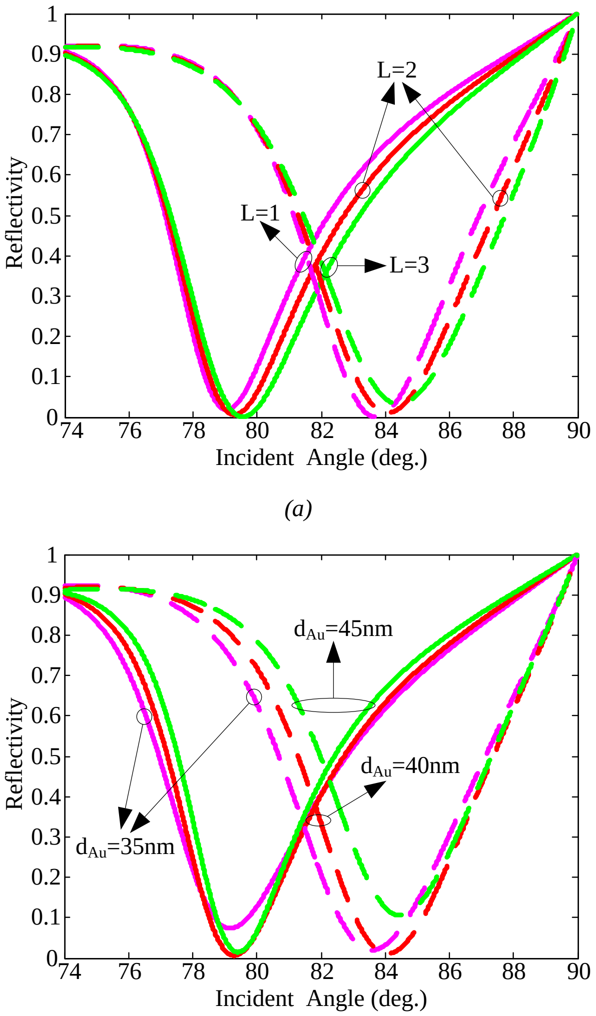

Fig. 3. SPR spectrum (a) for different number of graphene layer for L= 1, 2 and 3. (b) for different thickness of Au layer for d_{Au}= 35nm, 40nm and 45nm.The solid line spectrum and dash line spectrum stands for the refractive index of sensing medium n =1.324 and n =1.342 respectively (color online)

The effects of thickness of ZnO layer on SPR angle, for the two different glucose concentration, c =0g/L and c =100g/L, are shown as Fig. 4(b), where the thickness are 2nm, 40nm, 2×0.34nm for ITO, Au, Graphene respectively. It is viewed that, the SPR angle move towards the large angle both for c =0g/L and c =100g/L, that is, the SPR angle increases both for c =100g/L and c =0g/L, with the thickness of ZnO layer increasing. However, the SPR angle increases more for c =100g/L than that for 0g/L, as the thickness of ITO layer increase. Thus, the sensitivity is enhanced when the thickness of ZnO layer increase, but there is a better SPR peak at 3nm than that at other three thickness both for the two concentration limit. And it is obtained that the optimum thickness of ZnO layer is 3nm based on the enhancement of sensitivity.

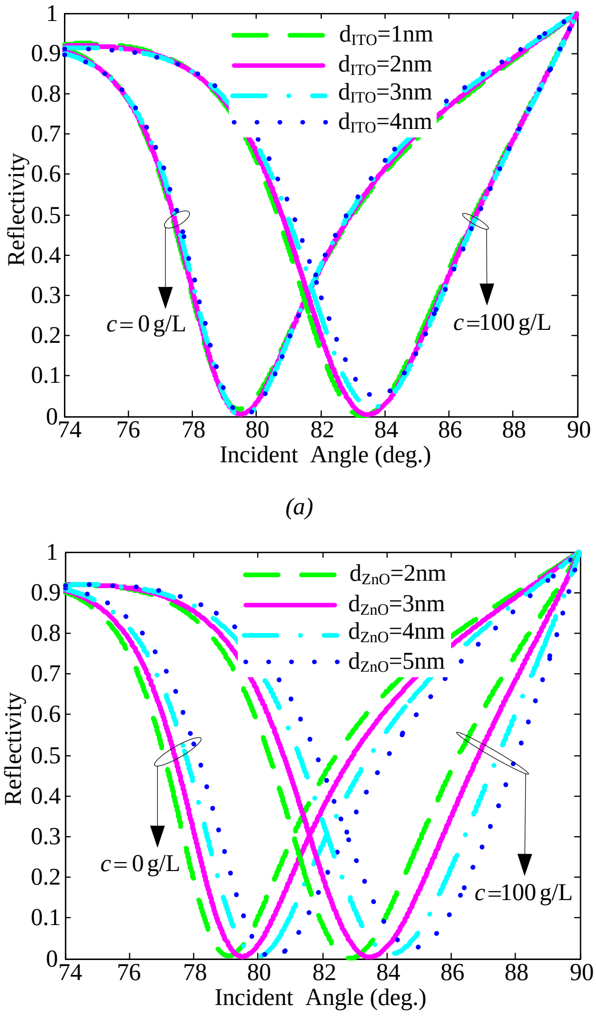

Fig. 4. The effect of (a) thickness of ITO layer (for d_{ITO} = 1nm, 2nm, 3nm and 4nm) on SPR angle, (b) thickness of ZnO layer (for d_{ZnO} = 2nm, 3nm, 4nm and 5nm) on SPR angle, for different glucose concentration, c =0g/L and c =100g/L (color online)

Thus, the thicknesses of 2nm, 40nm, 3nm and 0.68nm are chosen for ITO, Au, ZnO and Graphene respectively, for the structure designed. And the figure of merit, SPR spectrum for the glucose concentration, the effect of glucose concentration on the SPR spectrum for the structure designed is shown as Fig. 5, where the SPR spectrum for the glucose concentration, c=0g/L and c=100g/L, are given. Au nanowires array and two-dimensional nanomaterials, such as ITO, ZnO and Graphene, have extremely strong absorption properties. Besides, the combination of multi-layer muduim could show a better optical performance than single medium. Thus, the surface plasmon resonance effect can be greatly enhanced by them, so that the energy of the output light has a sharp drop at the position of the resonance angle. And the SPR spectrum changes because of the different glucose concentration. Concretely speaking, the SPR spectrum moves towards the higher glucose concentration, the SPR angle shifts to the higher glucose concentration correspondingly and increases significantly with the increasement of the glucose concentration.

The sensitivity of the SPR sensor or SPR glucose concentration sensor can be defined as

$$S_n = \frac{\Delta\theta_{SPR}}{\Delta n}, \quad S_e = \frac{\Delta\theta_{SPR}}{\Delta c} \tag{6}$$

where, $\triangle\theta_{SPR}$ is the change in resonance angle, $\triangle n$ is the the change in refractive index, $\triangle c$ is the change in glucose concentration, Sn and Se are the sensitivity of SPR sensor and SPR glucose concentration sensor respectively.

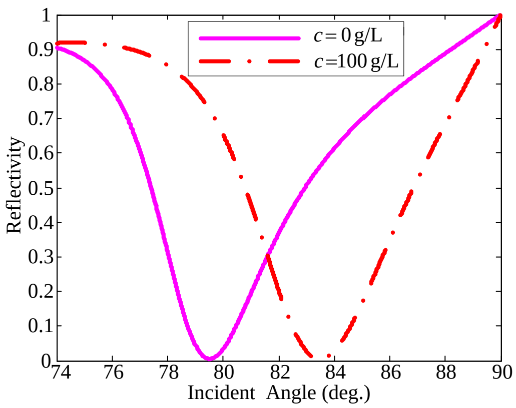

Fig. 5. SPR spectrum with different glucose concentration, C =0g/Land C =100g/L (color online)

The relationship between SPR angle and corresponding glucose concentration is given, as shown in Fig. 6, where the solid line stands for theoretical value, and the dot line stands for experiment value. It is showed that the SPR angle increases accordingly as the glucose concentration increases gradually, and there exists linear relationship between SPR angle and glucose concentration in the scope of glucose concentration, 0g/L conc.～100g/L conc.. Here, the reason why there exists linear relationship between SPR angle and glucose concentration, in the scope of glucose concentration, 0g/L conc.～100g/L conc.. It is because there exists a linear relationship between the refractive index and glucose concentration in the scope of glucose concentration, 0g/L conc.～100g/L conc.. The glucose concentration gradually increases in the scope of concentration, 0g/L conc.～100g/L conc., the refractive index also increases linearly with the glucose concentration correspondingly. So that SPR angle also increases linearly with the refractive index of glucose solution layer in the scope of glucose concentration, 0g/L conc.～100g/L conc..

Besides, the SPR angle shifts significantly, ranging from 79.44º to 83.39º, in the scope of glucose concentration, 0g/L conc.～100g/L conc.. Thus, the detection range of glucose concentration sensor is 0g/L～100g/L conc., the shift of SPR angle is 3.95º at the detection range, and also the sensitivity reached as high as 259.87º/RIU in terms of refractive index change, which has higher sensitivity compared with other sensor, such as the sensors with sensitivity of 59.5º/RIU[36], 75.0º/RIU[37], 83º/RIU[38], 121.67º/RIU[39], 181.95º/RIU[40] and 194º/RIU[41]. Then the sensitivity of SPR glucose concentration sensor reaches 0.0395º/(g/L)conc. in terms of glucose concentration detection.

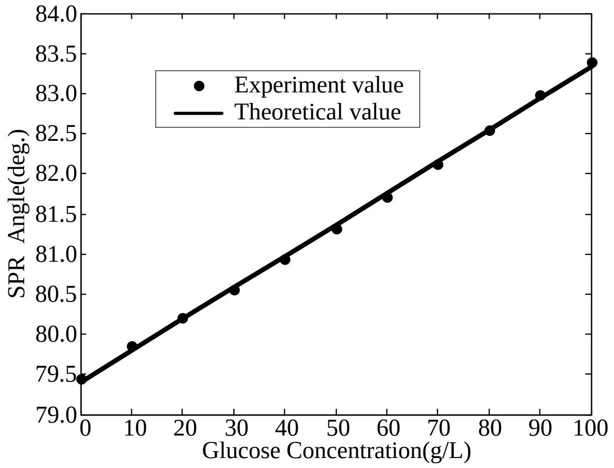

Fig. 6. Relationship between SPR angle and glucose concentration

4. Conclusion

In this paper, a novel prism coupling structure based on SPR is designed for the wide-range glucose concentration Sensor, and the thickness of each medium layer was optimized to get the good SPR spectrum and the high sensitivity. The sensitivity can reach as high as 259.87º/RIU in terms of refractive index change, and the sensitivity of SPR glucose concentration sensor reaches as high as 0.0395º/(g/L) conc. in the wide detection range of glucose concentration, 0g/L conc.～100g/L conc. And the relationship between SPR angle and glucose concentration is given, based on this, the making of a new optical detection device, SPR detecting device with a higher sensitivity, has a sufficient theoretical preparation.

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References

[1] V. P. Devanarayanan, V. Manjuladevi, R. K. Gupta, Sensors and Actuators B: Chemical **227**, 643 (2016).

[2] Preejith P. Vachali, Binxing Li, Alexis Bartschi, Paul S. Bernstein, Archives of Biochemistry and Biophysics **572**, 66 (2015).

[3]Anna Sankiewicz, Piotr Laudanski, Lech Romanowicz, Adam Hermanowicz, Wiesława Roszkowska-Jakimiec, Wojciech Debek, Ewa Gorodkiewicz, Analytical Biochemistry **469**, 4 (2015).

[4] J. C. Pickup, F. Hussain, N. D. Evans, O. J. Rolinski, D. J. Birch, Biosens. Bioelectron. **20**, 2555 (2005).

[5] Wolfgang Trettnak, Otto S.Wolfbeis, Analytica Chimica Acta **221**, 195 (1989).

6] P. Schläpfer, W. Mindt, P. H. Racine, Clinica Chimica Acta **57**, 283 (1974).

[7] Cheol Soo Park, Ko Keun Kim, Jong Min Choi, Kwang Suk Park, Physiological Measurement **28**, 583 (2007).

[8] Alen Pasic, Hans Koehler, Ingo Klimant, Lukas Schaupp, Sens. Actuators B: Chem. **122**, 60 (2007).

[9] William L. Barnes, Alain Dereux, Thomas W. Ebbesen, Nature **424**, 824 (2003).

[10] P. K. Maharana, S. Bharadwaj, R. Jha, J. Appl. Phys. **114**, 014304 (2013).

[11] Edy Wijaya, Cédric Lenaerts, Sophie Maricot, Juriy Hastanin, Serge Habraken, Jean-Pierre Vilcot, Rabah Boukherroub, Sabine Szunerits, Current Opinion in Solid State and Materials Science **15**, 208 (2011).

[12] J. Homola, S. S. Yee, G. Gauglitz, Sens. Actuator B **54**, 3 (1999).

[13] John S. Maier, Scott A. Walker, Sergio Fantini, Maria Angela Franceschini, Enrico Gratton, Optics Letters **24**, 2062 (1994).

[14] M. V. Sosnova, N. L. Dmitruk, A. V. Korovin, S. V. Mamykin, V. I. Mynko, O. S. Lytvyn, Appl. Phys. B **99**, 493 (2010).

[15] Ergun Simsek, Plasmonics **4**, 223 (2009).

[16] M. A. Schmidt, L. N. Prill Sempere, H. K. Tyagi, C. G. Poulton, P. St. J. Russell, Phys. Rev. B **77**, 033417 (2008).

[17] Ming-RuYang, Sheng Yuan Chu, Ren Chuan Chang, Sensors and Actuators B:

Chemical **122**(1), 269 (2007).

[18] Wan-Kyu Oh, HyeonseokYoon, Jyongsik Jang, Diamond and Related Materials **18**(10), 1316 (2009).

[19] Kyung Min Byun, Michael L. Shuler, Sung June Kim, Soon Joon Yoon, Donghyun Kim, Journal of Lightwave Technology **26**(11), 1472 (2008).

[20] Huijun Yao, Jinglai Duan, Dan Mo, Haci Yusuf Günel, Yonghui Chen et al., J. Appl. Phys. **110**, 094301 (2011).

[21] J. A. Kim, T. Hwang, S. R. Dugasani, R. Amin, R. Kulkarni, S. H. Park, T. Kim, Sens Actuators B Chem. **187**, 426 (2013).

[22] C. Rhodes, M. Cerruti, A. Efremenko, M. Losego, D. E. Aspens, J. P. Maria, S. Franzen, J. Appl. Phys. **103**, 1 (2008).

[23] C. Rhodes, S. Weibel, J. P. Maria, M. Losego, D. L. Leonard, B. Laughlin,G. Duscher, S. Franzen, J. Appl. Phys. **100**, 054905 (2006).

[24] J. B. Maurya, Y. K. Prajapati, Rajeev Tripathi, Silicon **10**, 245 (2018).

[25] R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, A. K. Geim, Science **320**, 1308 (2008).

[26] D. C. Elias, R. V. Gorbachev, A. S. Mayorov, S. V. Morozov, A. A. Zhukov, P. Blake, L. A. Ponomarenko, I. V. Grigorieva, K. S. Novoselov, F. Guinea, A. K. Geim, Nat. Phys. **7**, 701 (2011).

[27] X. L. Cheng, H. Zhao, L.H. Huo, S. Gao, J. G. Zhao, Sensors and Actuators B **102**, 248 (2004).

[28] M. Mahanti, D. Basak, Chem. Phys. Lett. **542**, 110 (2012).

[29] Sarika Shukla, Navneet K. Sharm, Vivek Sajal, Sensors and Actuators B **206**, 463 (2015).

[30] Rizwan Khan, Periyayya Uthirakumar, Kang-Bin Bae, See-Jong Leem, In-Hwan Lee, Materials Letters **163**, 8 (2016).

[31] Y. Ma, G. T. Du, S. R. Yang, Z. T. Li, B.J. Zhao, X. T. Yang, T. P. Yang, Y. T. Zhang, D. L. Liu, J. Appl. Phys. **95**, 6268 (2004).

[32] Rajneesh K. Verma, Banshi D. Gupta, J. Opt. Soc. Am. A **27**, 846 (2010).

[33] Pradeep Kumar Maharana, Rajan Jha, Srikanta Palei, Sensors and Actuators B **190**, 494 (2014).

[34] M. Caglar, Y. Caglar, S. Ilican, J. Optoelectron. Adv. M. **8**, 1410 (2006).

[35] J. W. Weber, V. E. Calado, M. C. M. van de Sanden, Applied Physics Letters **97**, 091904 (2010).

[36] Alka Verma, Arun Prakash, Rajeev Tripathi, Optics Communications **357**, 106 (2015).

[37] Munsik Choi, Nak-Hyeon Kim, Seyoung Eom, Tae Woo Kim, Kyung Min Byun, Hyeong-Ho Park, Thin Solid Films **587**, 43 (2015).

[38] J. B. Maurya,Y. K. Prajapati, V. Singh, J. P. Saini, Appl. Phys. A **121**, 525 (2015).

[39] Md. Biplob Hossain, Ibrahim Mustafa Mehedi, M. Moznuzzaman, Lway Faisal Abdulrazak, Md. Amzad Hossain, Results in Physics **15**, 102719 (2019).

[40] Maneesh Kumar Singh, Sarika Pal, Y. K. Prajapati, J. P. Saini, Materials Today: Proceedings **28**, 1776 (2020).

[41] Md Mahabubur Rahman, Md Masud Rana, Md Saifur Rahman et al., Optical Materials **107**, 110123 (2020).

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