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ORIGINAL ARTICLE

Sol-gel spin coating derived ZnO thin film to sense the acetic acid vapor

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Abstract

ZnO thin film of 80 nm thickness was deposited by the sol-gel spin coating method on SiO_2/Si substrate and subsequently post-annealed at 500 °C with a flow of oxygen for 60 min. Crystallographic structure of the sample was characterized by X-ray diffraction (XRD) method while a field emission scanning electron microscope (FESEM) was used to investigate the surface physical morphology and chemical composition. The sensitivity of the sample was tested to acetic acid vapor with different concentrations (20 ppm, 40 ppm, and 80 ppm) in the temperature range of 200-400 °C. The results showed that the ZnO thin film can be introduced as an acetic acid vapor sensor with a good reliability and detection limit of 20 ppm at the operating temperature of 320 °C.

Keywords: *Acetic acid; Sensitivity; Sol-gel; Thin film; ZnO.*

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INTRODUCTION

Acetic acid is a colorless volatile organic compound with the chemical formula of $C_2H_4O_2$ (CH_3COOH). It is widely used in the medical and food industries and as a solvent; however, there are many reports on the health effects of this compound. The effect of this compound, similar to other compounds, depends on the amount and the length of time a person is exposed. For example, prolonged skin contact with glacial acetic acid may result in tissue destruction. Inhalation exposure to acetic acid vapor at 10 ppm can produce some irritations of eyes, nose, and throat. In addition, some lung irritations may be resulted at 100 ppm [1-4]. Therefore, it seems that the development of a portable, fast and reliable sensor to detect the acetic acid vapor is necessary. In the last decade, the nano-structured ZnO has attracted the attention of numerous researchers due to its outstanding physical, chemical and sensing properties [5-10]. From the literature [5-7], it can be deduced that the nano-structured ZnO can be a good candidate to detect the volatile organic compounds (VOCs). Peng *et al.* [5] prepared the 3D flower-like hierarchical ZnO nanostructure by the hydrothermal method and investigated the sensitivity of the sample to different gases and vapors such as acetone, hydrogen, ethanol, methanol, formaldehyde, toluene and acetic acid. Muthukrishnan *et al.* [6] used the sol-gel dip coating method to obtain the ZnO thin films and investigated the sensitivity of the sample to acetone, ethanol and acetaldehyde. Luo et al [7] employed a hydrothermal method to prepare the mesoporous ZnO and Sn-doped ZnO thin films and studied the sensitivity of the samples to different volatile vapors including ethanol, methanol, acetone, formaldehyde and ammonia. Li et al [11] also used the chemical deposition method to prepare the pure ZnO and Sn-doped ZnO nano-structures on glass substrates and studied the ethanol and acetone sensing properties of the samples.

In contrast with the previous research and in order to more deeply understand of acetic acid sensing performance of the ZnO thin film, we have prepared the ZnO thin film by the sol-gel spin coating method and studied the nano-structure, sensitivity, reproducibility and stability of the mentioned sample as an acetic acid vapor sensor.

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EXPERIMENTAL

ZnO thin film of 80 nm thickness was deposited by sol-gel spin coating method on SiO_2/Si substrate. A domestic-made system was used to this goal. Prior to deposition, ultrasonically cleaned p-type Si(400) substrate with dimension of 3×3 cm^2 was oxidized in a horizontal tube furnace (Exciton, 1200-30/6, T.H, Iran equipped to Shinko temperature programmable controller – PCD 33A) with 200 standard cubic centimeter per minute (sccm) flow of oxygen gas at 1100°C to obtain SiO_2 layer.

0.45M Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) (98%) was mixed with isopropanol and was stirred at room temperature for 1h. When the solution turned milky, diethanolamine (DEA) was added slowly to yield a clear transparent homogeneous solution and the resulting mixture was further stirred for 1 h. After aging for 24 h, the solution was subjected to spin coating on the SiO_2/Si substrate [12-14]. The rotation speed of the coating unit was 2000 rpm and the duration of the single coating was 45 s. After deposition, in order to evaporate the solvent and organic residues as well as to achieve a good crystallinity, the ZnO thin film was post-annealed in the above mentioned tube furnace at the temperature of 500°C with an oxygen flow of 200 sccm for 60 min [15]. The thickness of the sample was also measured using an Alphastep profilometer. The sample was structurally characterized by means of a Philips x-ray diffractometer (X'pert multi-purpose diffractometer (MPD); CuKa radiation) with a step size of 0.02° and step time of 1 s while a field emission scanning electron microscope (FESEM) (Cam Scan MV2300, Czech & England) was used to investigate the physical surface morphology and chemical composition. In order to fabricate the gas-sensing element based on ZnO thin film, a pair of Au electrodes with dimensions of 3×3 mm^2 was deposited on the ZnO thin film by the e-beam evaporation method using a mask made for this application. To measure the response of the sample, it was positioned on a hot plate inside an airtight stainless steel chamber (a domestic-made system). A DC power supply was used to supply the current to the heat elements of the hot plate. The operation temperature of the sensor was measured by a thermocouple mounted on the substrate. The electrical resistance of the sample was measured in air and presence of acetic acid vapor (20 ppm, 40 ppm, 80 ppm) in the temperature range of 200-400°C. Schema and set-up of the gas sensing measurement system and the calculating method of concentration and injection volume for the vapor are given in [7, 15], respectively. Response or sensitivity (S) is defined as the ratio of R_a/R_g ($S=R_a/R_g$) where R_a and R_g are the resistance of metal oxide semiconductors in air and the presence of reducing vapors, respectively [12]. Response or recovery time is also estimated as the time taken for the sensor output to reach 90% of its saturation after applying or switching off the target gas in a step function [12].

RESULTS AND DISCUSSION

Structural analyses

X-ray diffraction (XRD) pattern of the ZnO thin film produced in this research is shown in Fig. 1. It can be observed that the sample shows three peaks belonging to ZnO(100), ZnO(002), ZnO(101) crystallographic orientations attributed to the Wurtzite structure (with reference to JCPDS Card no.: 36–1451, symmetry: hexagonal P and space group: P63mc). This crystallographic structure is in agreement with the crystallographic structure reported by many researchers who used different chemical and physical preparation methods [5-8, 11-16]. However, there are some differences in preferred orientation and peak intensity that can be attributed to the substrate and the preparation parameters and process.

Fig. 2 shows the energy dispersive X-ray (EDX) spectrum of the ZnO thin film prepared in this work. It can be seen that the result shows the atomic ratio of 1.15 for O/Zn (O: 53.60 at(%), Zn: 46.40 at(%)). It is well-known that the ZnO can be formed in various shapes such as nanowire, nanobelt, nanorod, nanosheet, and granular [12,16-19], and all these shapes are affected by the growth methods and deposition parameters. FESEM micrograph of the ZnO thin film produced in this work is also shown in Fig. 3. It can be observed that the image exhibits a uniform-granular structure with visible separated grains.

Sensing analyses

First step of the sensing analyses was the determination of the operating temperature. The operating temperature of a gas sensor is usually the temperature that corresponds to the maximum sensitivity [12]. To this end, the ZnO thin film prepared in this work was exposed to

acetic acid vapor (80 ppm) in the temperature range of 200-400 °C at increments of 40°C. The result of this measurement is shown in Fig. 4. From this curve, it can be deduced that the highest response is obtained at 320 °C. Decreasing of the sensitivity after the temperature of 320 °C can be related to increasing the concentration of carriers of metal oxide semiconductor by increasing the temperature; however, it should be noticed that the adsorption, desorption and reaction energies of various gases and vapors are different.

Detection limit is the lowest amount of the object/vapor that the sensor can detect [12]. After defining the operating temperature, in order to characterize the detection limit, the sample was exposed to high-purity acetic acid with different concentrations of 20 ppm, 40 ppm and 80 ppm at the operating temperature of 320 °C.

Fig. 5 depicts the dynamic response of the ZnO thin film produced in this work to acetic acid vapor with different concentrations at the operating temperature of 320°C. The results obtained from these curves, namely response, response time and recovery time, are shown in Fig. 6. It can be seen that the sample shows the response values of 2, 5.5 and 9.5 for 20 ppm, 40 ppm and 80 ppm of acetic acid vapor at the operating temperature of 320 °C, respectively. In addition to this, it can be observed that the response time is decreased by increasing of vapor concentration while the recovery time is increased.

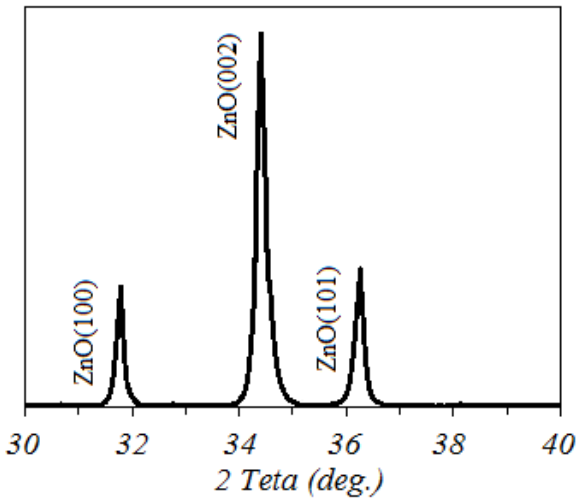

Fig. 1: X-ray diffraction (XRD) pattern of the ZnO thin film derived by sol-gel spin coating method.

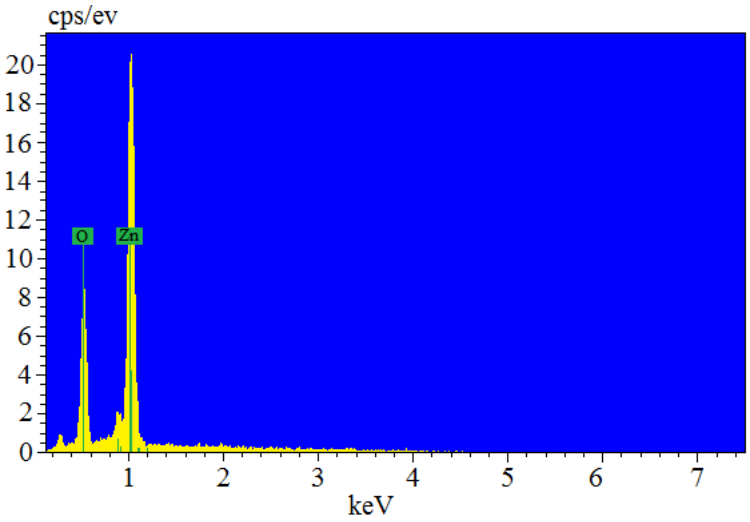

Fig. 2: Energy dispersive X-ray (EDX) spectrum of the ZnO thin film derived by sol-gel spin coating method.

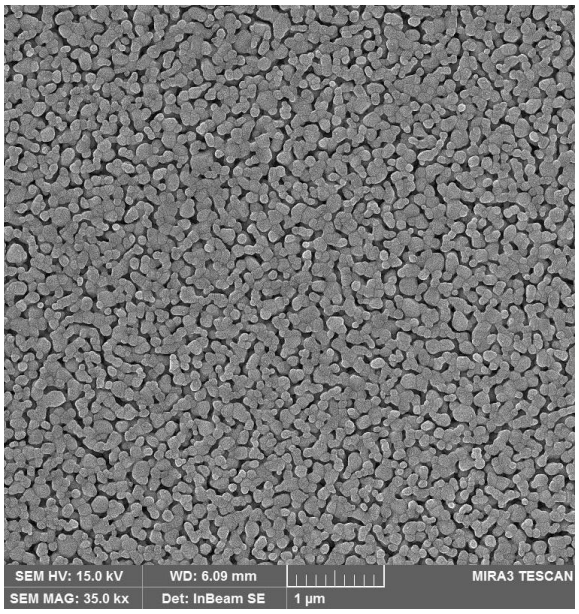

Fig. 3: FESEM micrograph of the ZnO thin film derived by sol-gel spin coating method.

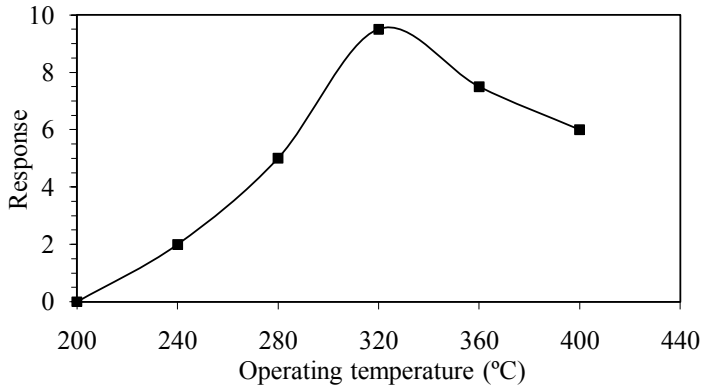

Fig. 4: Response of the ZnO thin film derived by sol-gel spin coating method to the acetic acid vapor (80 ppm concentration) as a function of temperature in the range of 200-400 °C.

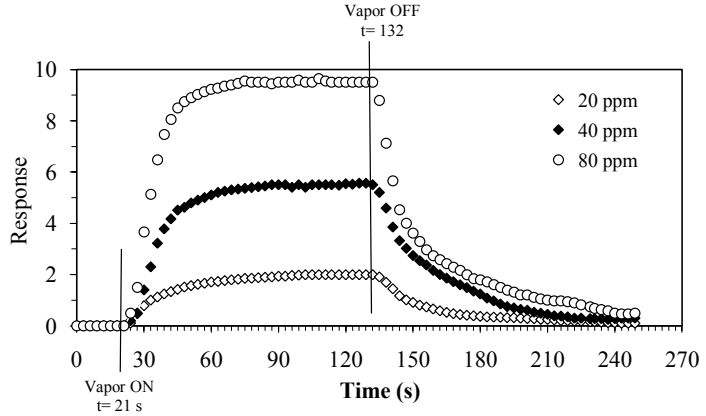

Fig. 5: Dynamic response of the ZnO thin film derived by sol-gel spin coating method for different concentrations of acetic acid vapor at the operating temperature of 320 °C.

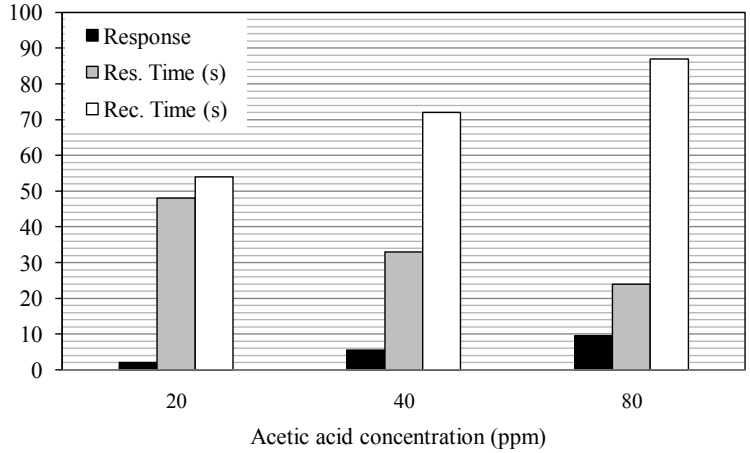

Fig. 6: Response, response time and recovery time of the ZnO thin film derived by sol-gel spin coating method as a function of acetic acid concentration at the operating temperature of 320 °C.

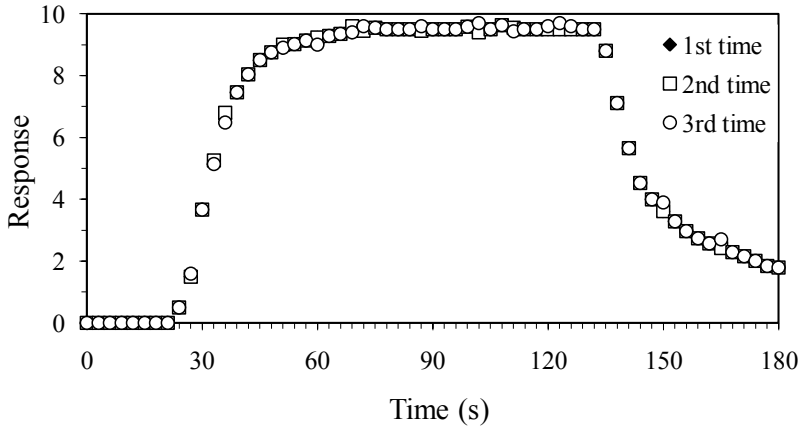

Fig. 7: Dynamic response of the ZnO thin film derived by sol-gel spin coating method to 80 ppm acetic acid vapor at the operating temperature of 320 °C for three times, a test for reproducibility of sensor.

It is expected that an increase in the acetic acid concentration provide more vapor molecules to be adsorbed on the sample surface per unit time, which in turn increases the response and decreases the response time, hence sensitivity will improve. Furthermore, by increasing the number of atoms adsorbed on the surface of the sensor, the necessary time to desorb (*i.e.* recovery time) becomes longer [12]. After it became clear that the ZnO thin film produced in this work may be a suitable sensor to detect the acetic acid vapor, reproducibility and stability of the ZnO thin film based acetic acid sensor were tested at the operating temperature of 320 °C.

In order to investigate the reproducibility of the ZnO thin film based acetic acid sensor, the response of the sample was tested to 80 ppm acetic acid vapor at the operating temperature of 320 °C for three times. These results are depicted in Fig. 7 that show good reproducibility of the sample. In order to study the stability of the sample, the response of the ZnO thin film prepared in this work to acetic acid vapor (80 ppm) at the operating temperature of 320 °C was measured as a function of day in steps of 3 days for 18 days. Fig. 8 depicts the results of this test. It can be seen that the response of the sample decreases from 9.5 to 7.5 with the time lapse (namely ~ 79% stability). The mentioned reduction of the response may be related to the reaction of the film surface with its surrounding especially humidity during and between the measurements [20, 21].

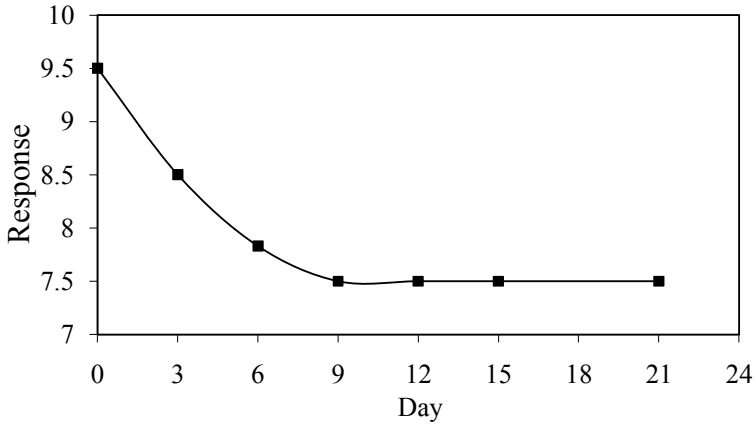

Fig. 8. Electrical response of the ZnO thin film derived by sol-gel spin coating method to 80 ppm acetic acid vapor at the operating temperature of 320 °C as a function of day, a test for stability of the sample.

CONCLUSION

ZnO thin film (thicknesses: 80 nm) was deposited by the sol-gel spin coating method on the SiO_2/Si substrate and subsequently post-annealed at 500°C in order to achieve a good crystallinity. The sample was structurally, chemically and morphologically characterized by XRD and FESEM. The response of the sample was tested to acetic acid vapor with different concentrations (20 ppm, 40 ppm, and 80 ppm) in the temperature range of 200-400 °C. The results showed that the best response of the ZnO thin film prepared in this work to acetic acid vapor was achieved at the operating temperature of 320°C. The prepared ZnO thin film based acetic acid sensor also showed a good reproducibility and stability as well as the detection limit of 20 ppm at the operating temperature of 320°C.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES

[1] Dean J. A., (1985), *Lange's Handbook of Chemistry.* New York: McGraw-Hill.

[2] Sell C., (2006), The Chemistry of Fragrances: From Perfumer to Consumer. Cambridge, UK: *Royal Society of chemistry (RSC).*

[3] Bernthsen A., (1992), Organic chemistry. London: Blackie and Son.

[4] http://www.inchem.org/documents/icsc/icsc/eics0363.htm.

[5] Peng C., Guo J., Yang W., Shi C., Liu M., Zheng Y., Xu J., Chen P., Huang T., Yang Y., (2016), Synthesis of three-dimensional flower-like hierarchical ZnO nanostructure and its enhanced acetone gas sensing properties. *J. Alloy. Compd.* 654: 371-378.

[6] Muthukrishnan K., Vanaraja M., Boomadevi S., Karn R. K., Singh V. , Singh, P. K. , Pandiyan K., (2016), Studies on acetone sensing characteristics of ZnO thin film prepared by sol-gel dip coating. *J. Alloy. Compd.* 673: 138-143.

[7] Luo S., Shen Y., Wu Z., Cao M., Gu F., Wang L., (2016), Enhanced ethanol sensing performance of mesoporous Sn-doped ZnO. *Mater. Sci. Semicond. Process.* 41: 535-543.

[8] Lakshmipriya V., Natarajan B., Jeyakumaran N., Prithivikumaran N., (2014), Effect of annealing and UV illumination on properties of nanocrystalline ZnO thin films. *Int. J. Nano Dimens.* 5: 479-487.

[9] Mastali N., Bakhtiari H., (2014), Investigation on the structural, morphological and photochemical properties of spin-coated TiO_2 and ZnO thin films prepared by sol-gel method. *Int. J. Nano Dimens.* 5: 113-121.

[10] Yan L., Dong-Li L., Jin-Cheng L., (2015), Optical and gas sensing properties of mesoporous hollow ZnO microspheres fabricated via a solvothermal method. *Chinese Chem. Lett.* 26: 304-308.

[11] Li X., Chang Y., Long Y., (2012), Influence of Sn doping on ZnO sensing properties for ethanol and acetone. *Mater. Sci. Eng. C.* 32: 817-821.

[12] Teimoori F., Khojier K., Dehnavi N. Z., (2016), Investigation on the electrical and methane gas-sensing properties of ZnO thin films, produced by different methods. *J. Electron. Mater.* 45: 4881-4889.

[13] Bhattacharyya P., Basu P. K., Saha H., Basu S., (2007), Fast response methane sensor using nanocrystalline zinc oxide thin films derived by sol–gel method. *Sens. Actuat. B*. 124: 62-67.

[14] Bhattacharyya P., Mishra G. P., Sarkar S. K., (2011), The effect of surface modification and catalytic metal contact on methane sensing performance of nano-ZnO–Si heterojunction sensor. *Microelec. Reliab.* 51: 2185-2194.

[15] Khojier K., Savaloni H., (2015), Improving the H_2 gas sensitivity of ZnO thin films by modifying the annealing conditions. *J. Electron. Mater.* 44: 3458-3464.
[16] Khojier K., Savaloni H., Amani E., (2014), Influence of annealing conditions on the crystallographic structure, chemical composition and luminescence of ZnO thin films. *Appl. Surf. Sci.* 289: 564-570.
[17] Bie L. J., Yan X. N., Yin J., Duan Y. Q., Yuun Z. H., (2007), Nanopillar ZnO gas sensor for hydrogen and ethanol. *Sens. Actuators B.* 126: 604-608.
[18] Choopun S., Hongsith N., Mangkorntong P., Mangkorntong N., (2007), Zinc oxide nanobelts by RF sputtering for ethanol sensor. *Physica E*. 39: 53-56.
[19] Kim H. W., Shim S. H., Lee C., (2007), Effects of thermal annealing on the properties of ZnO-coated MgO nanowires. *Mater. Sci. Eng. B*. 136: 148-153.
[20] Zolghadr S., Khojier K., Kimiagar S., (2016), Study of sensitivity and selectivity of α-Fe_2O_3 thin films for different toxic gases and alcohols. *Mater. Sci. Semicond. Proc.* 54: 6-13.
[21] Bandgar D. K., Navale S. T., Khuspe G. D., Pawar S. A., Mulik R. N., Patil V. B., (2014), Novel route for fabrication of nanostructured α-Fe_2O_3 gas sensor. *Mater. Sci. Semicond. Process.* 17: 67-73.