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Synthesis of Cu_2ZnSnS_4 (CZTS) Semiconductor Thin Film with Variation of Sulfur Solution Concentration

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Abstract: The Cu_2ZnSnS_4 (CZTS) thin film is an alternative semiconductor material as a light absorbing layer in solar cells. The advantages of CZTS as a light absorbing layer are the availability of abundant materials in nature and high absorption coefficient values. The absorbent layer was prepared using the sol-gel and spin coating method on an indium tin oxide (ITO) glass substrate. Films were made with a sol-gel solution with varying concentrations of sulfur solution, namely with a concentration of 3M and 6M using a simple spin coating tool which was rotated for 30 seconds. The film formed was hardened at 550°C for 60 minutes under N_2 gas. The results of X-ray diffraction analysis showed that the CZTS thin films formed from the two samples had a kesterite crystal structure with a small percentage. Samples with a sulfur solution concentration of 6M had a higher percentage of crystals with a percentage of 13.26% with a film thickness of 3.73-4.73 µm, while the sulfur solution concentration of 3M has a percentage of 7.54%. The CZTS thin film sample with 6M sulfur concentration has a bandgap energy of 1.88 eV and the absorption coefficient value obtained is 5 x $10^3 cm^{-1}$ which is the best result. In conclusion, the spin coating method has the potential to be used to produce kesterite ZCTS under relatively high concentrations of sulfur solution.

Keywords: CZTS thin films, casterite, semiconductors, spin coatings, sulfur

Abstrak: *Film tipis Cu_2ZnSnS_4 (CZTS) merupakan bahan alternatif semikonduktor sebagai lapisan penyerap cahaya pada sel surya. Kelebihan CZTS sebagai lapisan penyerap cahaya ialah ketersediaan bahan yang berlimpah di alam dan nilai koefisien absorpsi yang tinggi. Lapisan penyerap dibuat dengan menggunakan metode sol-gel dan spin coating pada substrat kaca indium timah oksida (ITO). Film dibuat dengan larutan sol-gel dengan variasi konsentrasi larutan sulfur yaitu dengan konsentrasi 3M dan 6M menggunakan alat spin coating sederhana yang diputar selama 30 detik. Film yang terbentuk dikeraskan pada suhu 550 °C, selama 60 menit dengan dialiri gas N_2. Hasil analisis difraksi sinar X menunjukkan bahwa film tipis CZTS yang terbentuk dari kedua sampel memiliki struktur kristal kasterit dengan persentase yang kecil. Sampel dengan larutan sulfur konsentrasi 6M memiliki jumlah persen kristal yang lebih tinggi dengan persentase 13,26 % dengan ketebalan film 3,73- 4,73 µm, sedangkan larutan sulfur konsentrasi 3M memiliki persentase 7,54%. Sampel film tipis CZTS dengan konsentrasi sulfur 6M memiliki energi celah pita sebesar 1,88 eV dan nilai koefisien absorpsi yang diperoleh sebesar 5 x $10^3 cm^{-1}$ yang merupakan hasil terbaik. Sebagai kesimpulan, metode spin coating berpotensi digunakan untuk menghasilkan ZCTS fase kasterit pada kondisi konsentrasi larutan sulfur yang relatif tinggi.*

Kata kunci: *film tipis CZTS, kasterit, semikonduktor, spin coating, sulfur*

INTRODUCTION

Solar panels are a combination of several solar cells that are very small and thin, either in series, parallel or a mixture (series and parallel) (Ramadhan *et al.* 2016). On solar panels there are several solar cells that can convert sunlight energy into electrical energy (Sharma *et al*. 2015). The electrical energy produced by solar panels from solar radiation can reach 1000 Watt/m^2 on a bright midday day (Martinez *et al*. 2017). If a 1 m^2 semiconductor device has an efficiency of 10%, then this solar cell module is capable of producing 100 Watts of electrical energy. Electrical energy is produced from sunlight absorbed by the absorber in the solar cell. Materials that can be used as solar cell absorbers, namely silicon wafers which are first generation solar cells. Silicon wafer material is the dominant technology in the commercial production of solar cells, accounting for more than 86% of the solar cell market. Silicon solar cells are dominant due to their high efficiency, although production costs are quite high (Cantas *et al.* 2018). The second-generation solar cells are based on photon absorption layers arranged in layers. This combination can absorb more light and each layer uses a thin film material that can reduce the mass of solar cell materials. Usually, the efficiency value of thin film solar cells is lower compared to silicon-based solar cells which reaches 26.6%, but the production cost also decreases. The materials for second generation solar cells that have good quality are cadmium telluride (CdTe), and Copper indium gallium selenide (CIGS). According to Mamta *et al.* (2022), the efficiency of CdTe and CIGS absorbers is 22% and 20% respectively. However, these absorber materials are toxic metals and are rarely available in nature (Jirage & Bhuse 2019).

One alternative material for making thin film absorbers is Cu_2ZnSnS_4 (CZTS). CZTS is a semiconductor material made of copper, zinc, tin, and sulfur. These materials are abundant on earth, cheap, and environmentally friendly. Although the efficiency of CZTS currently only reaches 12.7%, CZTS has a band gap energy of 1.0–1.5 eV (Pawar *et al.* 2010). The band gap value is an ideal value for converting some energy from the solar spectrum into electrical energy. CZTS also has a high absorption coefficient value, which is around 10^4 cm^{-1} in the visible light spectrum region and only requires a layer thickness of several microns to absorb all photons with energy above its band gap. Therefore, Cu_2SnZnS_4 is a promising absorber material for application in photovoltaic cells in large-scale and sustainable solar energy absorption (Rahman *et al.* 2021). The growth of CZTS thin films was carried out using the sol-gel method and spin coating growth. The sol-gel process consists of the chemical transformation of a liquid (sol) into a gel state with subsequent treatment and transition into a solid oxide material. The main advantages of the sol-gel process are that high purity and nanostructures can be achieved at low temperatures (Bokov *et al.* 2021).

This research was conducted to synthesize CZTS solution using the sol-gel method with variations in sulfur solution concentration and study the growth of thin layers using the spin coating technique. The technique used to grow thin layers was the spin coating technique, the easiest and fastest technique for growing thin layers. The thin layer produced by the spin coating method has a fairly high level of homogeneity. The desired coating thickness can be controlled based on the time and rotation speed of the spin coater tool. The spin coating process includes 4 stages consisting of deposition, spin up and spin off as well as the evaporation stage which determines the final thickness of the thin layer produced from the sol-gel technique with the spin coating method which will produce a thin layer with quite high quality and also relatively cheap manufacturing costs. (Tyona 2013). The process of growing CZTS thin films also used a sulfur solution ratio because sulfurization is an important process for growing high-quality CZTS thin films, because the morphological, compositional and structural properties of CZTS thin films and the parameters of solar cell devices are greatly influenced by sulfur compounds during the CZTS formation process (Zhang *et al.* 2019).

MATERIALS AND METHOD

Materials

The materials used in this study include $CuSO_4.5H_2O$ (Merck Jerman), $ZnSO_4.7H_2O$ (Merck Jerman), $SnSO_4$ (Ajax Finechem Australia), $Na_2S_2O_3.5H_2O$ (Merck Jerman), $C_6H_5Na_3O_7.2H_2O$ (Merck Jerman), ion-free water, N_2 gas, and Indium Tin Oxide glass (ITO) 10 Ω 1,0 cm x 2,0 cm x 1,1 mm.

Methods

CZTS sol-gel solution was prepared by mixing 2 mL of 3 M $Na_2S_2O_3.5H_2O$ (or 6 M), 2 mL of 2,5 M $CuSO_4.5H_2O$, 1 mL of 2 M $ZnSO_4.7H_2O$, 1 mL of 1,5 M $SnSO_4$, and 1 mL of 0,4 M $C_6H_5Na_3O_7.2H_2O$. The solution is then stirred and heated at a temperature of 40 ºC using a hot plate and magnetic stirrer for 15 minutes or until the solution is homogeneous (Pawar *et al.* 2012). Next, the sol-gel solution was dripped onto the ITO glass substrate, which had previously been cleaned and placed into a simple spin coating tool, using a dropper pipette as much as 3 drops with a rotation of 2500–3000 rpm for 30 seconds. The simple spin coating tool used in this study was assembled by using a dynamo with a rotation value of 2500-3000 rpm, and a bottle cap. Furthermore, the film that has been formed is hardened by heating (annealing) using a furnace. The film was placed in a porcelain dish filled with N_2 gas for 45 minutes at a temperature of 550 ºC (Zhang *et al.* 2019). The *kasterite* crystals resulting from the hardening process were further analyzed by XRD (crystal phase), SEM-EDX (film thickness), and UV-visible spectrophotometer (band gap energy and absorption coefficient).

RESULT AND DISSCUSION

CZTS thin film

The sol gel method is used because it can produce particles that have a uniform shape and small size with an even distribution of metal (Tranquillo & Bollino 2020). In the sol-gel method, electrolyte solutions containing Cu, Zn, and Sn elements are mixed with distilled water with concentrations of 2.5 M; 2 M; and 1.5 M respectively, while for the S element, it is made with two concentration variations of 3 M and 6 M and is given a code according to the sulfur ratio with the codes CZ3M and CZ6M to see the comparison of the percentage of kasterite crystals formed. Mixing the sol-gel solution produces a homogeneous solution and the color of the solution changes to green (Figure 1) with the CZ3M sample

(a) (b)

Figure 1 Sol-gel solution of sample (a) CZ3M and (b) CZ6M

being lighter compared to the CZ6M sample which tends to be darker.

The spin coating method is used to deposit a thin layer by dripping the material in the form of a solution onto the center-top surface of the substrate stored on a rotating disk either manually or with the help of a robot. The solution can be attracted to the edge of the substrate and spread evenly by utilizing the centripetal force that appears when the substrate is rotated at a high rotational speed (Tyona 2013). When the spin coater is at a constant rotation speed, some of the excess solution will go to the edge of the substrate and will be released from the substrate so that the solution layer on the substrate will become thinner. The concept of motion in the spin coating method is a circular motion. When an object moves in a circle, there is a centripetal force and an imaginary centrifugal force in the horizontal direction. While in the vertical direction there is a gravitational force that will produce friction between the substrate and the solution that can appear when there is acceleration of rotation on the spin coater tool, where the direction of the friction force is in the same direction as the rotation of the solution that is undergoing the spin coating process. In the spin coating method, friction is a secondary force whose value and influence can be ignored. The spin coating tool used is a simple tool that is assembled by yourself with a dynamo and a bottle cap as the rotating tool (Figure 2).

The spin coating film was hardened by heating the film sample to a temperature of 550°C in a furnace filled with nitrogen gas. The crystallization process will take place if the hardening temperature is around 350–550°C, and the optimal temperature for the hardening process is at 550°C (Emrani *et al*. 2013). The temperature range will strengthen the metal bond with the substrate so that the substrate surface becomes smoother and more transparent. On the other hand, if the hardening temperature is below 350 °C, it will not cause a crystallization process, so that an amorphous structure is formed, the metal is not strongly bound to the substrate, and allows the entry of oxygen or free air which can form other unwanted compounds (Rajeshmon 2013). The results of the film hardening process at a temperature of 550 °C are shown in Figure 3. The film on the surface of both glass substrates looks transparent, but CZTS precipitate grains are still visible in the center of the surface of the glass substratet. This happens because the spin coating technique used is still not even, one of the main factors can be caused by the use of a simple spin coating tool that is not 180° straight. However, it can also be suspected that the non-uniformity of the grain size on the substrate surface is caused by the lack of homogeneity of the sol-gel solution produced. Although all the metal salts used have fairly good solubility in water, their solubility can be affected by the effect of the common ion of the sulfate anion.

Characteristics of CZTS thin film

The crystal characterization of the CZTS film for the CZ3M and CZ6M samples using XRD can be seen in Figure 4. The XRD diffractogram shows that both films have absorption peaks, indicating the presence of crystals formed. However, the CZTS film of the CZ3M sample solution appears to have fewer peaks compared to the CZTS film of the CZ6M sample solution. This indicates that the CZTS film of the CZ3M sample solution is still largely amorphous, and the sulfur solution concentration of 3 M is less suitable for producing the desired CZTS crystal structure.

Based on the results of XRD analysis, the CZ3M sample shows the highest peak with a Miller index value (112) at 2θ 28.44° with a percentage of 2.6456%, while the Miller index (200), and (312) at 2θ 32.93° and 56.06° have a percentage below 2% with a total casterite crystal of 7.36%. According to Pawar *et al*. (2010), CZTS has a casterite crystal structure with Miller indices 112, 200, 220, and 312, which correspond to 2θ of CZTS according to JCPDS 26–0575. Meanwhile, the results of the analysis of the CZ6M sample with the highest intensity with the Miller index value corresponding to the CZTS phase are shown by the index (200) at 2θ 32.93° with a percentage of 4.85%, while the Miller indexes (112), (220), and (312) at 2θ 28.35°; 33.02°; and 56.06° have a percentage of around 1% with a total casterite crystal of 13.26%.

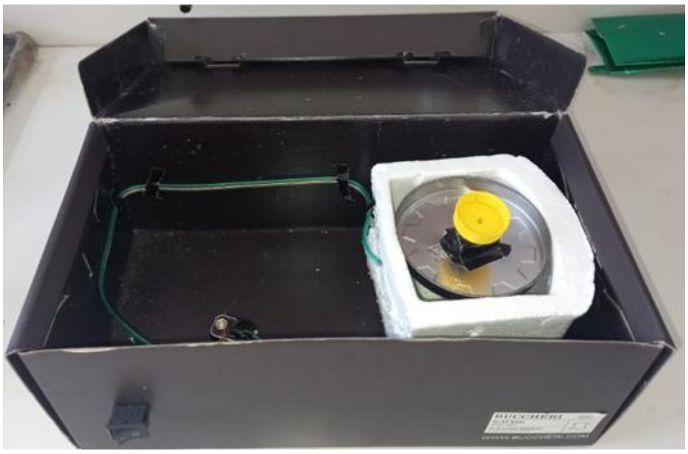
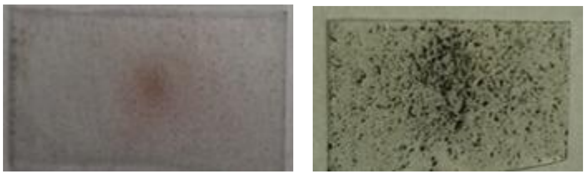
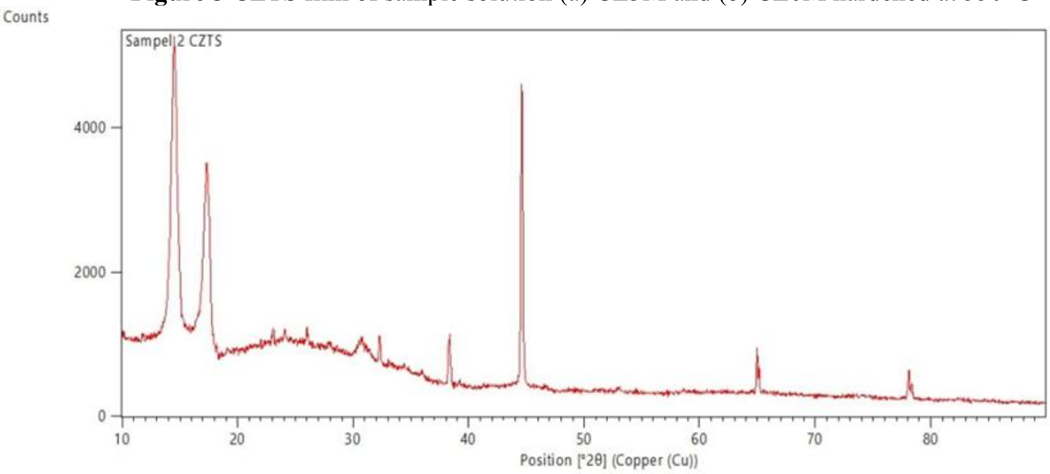


Figure 2 Self-assembled spin coating tool

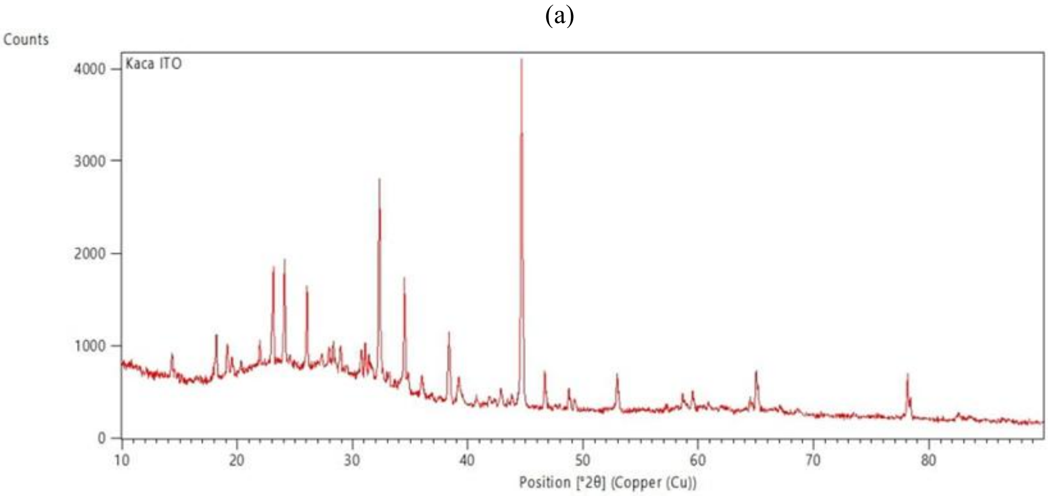


(a) (b)

Figure 3 CZTS film of sample solution (a) CZ3M and (b) CZ6M hardened at 550°C



(a)



(b)

Figure 4 Diffractograms of CZTS films of samples (a) CZ3M and (b) CZ6M

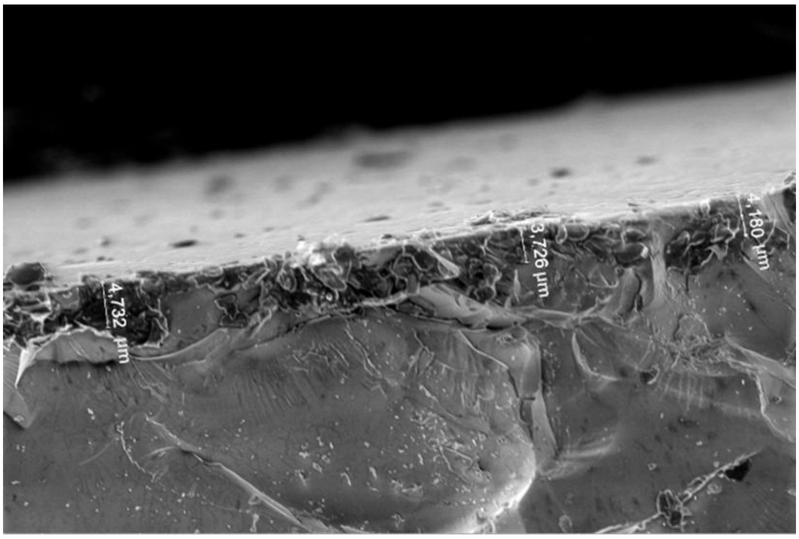


Figure 5 SEM image of cross-section of sample CZ6M

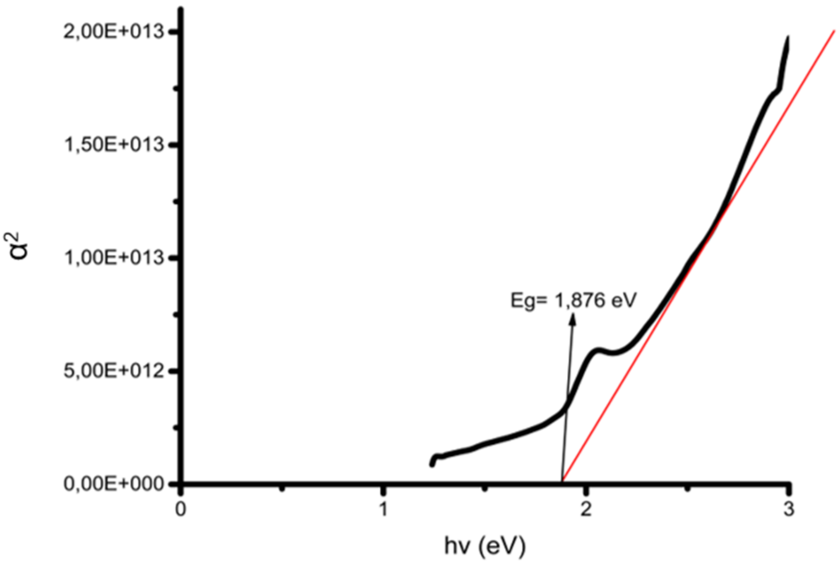


Figure 6 Band gap energy of CZ6M sample

The percentage of Cu_2ZnSnS_4 compound formed in the sample concentration solution CZ6M is greater than in the sample concentration solution CZ3M. It can be concluded that increasing the concentration of sulfur solution also increases the number of Cu_2ZnSnS_4 crystals formed. However, further studies are needed to obtain the optimum concentration of sulfur solution required for CZTS synthesis. The resulting kesterite crystals are higher than those obtained by Sugiarti *et al*. (2018), who produced a kesterite percentage of 7.3% using the electrodeposition technique. The peak with the highest intensity in this study (Figure 4) appeared at 2θ 44.9°, which is suspected to be Cu_9S_5 (JCPDS 023–0962). Another identifiable peak was at 2θ 37.3°, which according to JCPDS 80–0020 is the compound ZnS.

The emergence of the dimer compound is thought to be due to the time and temperature of crystal hardening not being optimal. According to the reaction mechanism for the formation of the Cu_2ZnSnS_4 compound, the first compound formed is Cu_2S. This compound is easily formed, even without a hardening process, because its formation temperature is below 100°C. After the Cu_2S compound is formed, the ZnS compound will then form followed by the formation of the SnS_2 compound. The Cu_2S compound that was formed at the beginning will then react with the SnS_2 compound to form the Cu_2SnS_3 compound which will then react with the ZnS compound to form the Cu_2ZnSnS_4 compound (CZTS) at an optimum formation temperature of more than 350°C (Kattana *et al*. 2015).

Morphological observations of CZTS films were conducted using a scanning electron microscope (SEM). The CZTS films tested in this study were only samples with the highest percentage of kesterite crystals, namely sample CZ6M. Based on the SEM results (Figure 5), the CZTS film that was made had an uneven thickness with a value between 3.73 to 4.73 µm. This is because the spin coating technique used was not optimal, resulting in an uneven coating, and the resulting sol-gel solution was not very homogeneous and may have been thicker than expected. Therefore, further research on the effect of solution viscosity is needed to ensure even coating results. According to Benami (2019), the ideal film thickness for semiconductor thin films from CZTS is around 2 µm.

Optical Characteristics of CZTS Film

The band gap energy and absorption coefficient of the film were determined using a UV-Vis spectrophotometer. This test was conducted to determine the optical behavior of the material in response to high-intensity sunlight. The band gap energy itself is the energy required to excite electrons from the valence band to the conduction band. The results of measurements and calculations of the band gap energy on the CZ6M sample obtained a value of 1.876 eV (Figure 6). This indicates that the resulting CZTS sample is still suitable for use as a semiconductor material for absorbing sunlight in the visible light region. However, based on XRD data, the majority of the phases formed in the synthesized crystal film are not CZTS, so the value is mostly contributed by secondary phases such as CuS and ZnS. In addition to measuring the band gap energy, the absorption coefficient value of the CZTS sample was also determined and obtained a value of 29,49 x 10^4 cm^{-1}. According to Haghighi *et al.* (2018), the ideal absorption coefficient for light-absorbing materials is greater than 10^4 cm^{-1}. The higher the absorption coefficient of a material, the better the electrical energy produced because the material will more easily absorb solar energy.

CONCLUSION

Kesterite crystal growth was successfully achieved using the sol-gel and sipn coating methods with varying sulfur concentrations on an ITO glass substrate. The resulting CZTS thin films of CZ3M and CZ6M sample solutions had kesterite crystal percentages of 7.36% and 13.26%, respectively. The CZ6M sample had a film thickness of 3.726–4.732 µm, which is twice the ideal semiconductor film thickness for solar cells.

The band gap energy value of 1.876 eV and the absorption coefficient of 29,49 x 10^4 cm^{-1} indicate that the synthesized CZTS films remain promising as light-absorbing materials.Overall, the sol–gel and spin-coating approaches demonstrate potential for the growth of kesterite-phase CZTS crystals, although further optimization is required to improve phase purity and film thickness.

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