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FABRICATION OF $Sr_{1-x}Ba_xBi_4Ti_4O_{15}$ THIN FILMS FOR PIEZOELECTRIC PRESSURE SENSORS

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ABSTRACT

This paper reports the fabrication of Strontium Barium Bismuth Titanate $Sr_{1-x}Ba_xBi_4Ti_4O_{15}$ (SBBT) thin films for piezoelectric pressure sensors. The SBBT films and capacitance devices with structure of Al/TiO_2/SBBT/TiO_2/SiO_2/Si were fabricated using sol-gel technique. The microstructure of SBBT thin films have been systematically studied in as-prepared (un-annealed) condition as well as after annealing at 500 C for 2 mins. The general trend seems to indicate that the annealed samples showed better piezoelectric properties. X-ray diffraction patterns reveal changes of crystalline structure after annealing. Another important parameter is dielectric constant, which is found toward higher value after annealing. For the sensor device measurement, the SBBT thin film pressure sensors were tested by pneumatic loading method at pressure range between 0 to 450 kPa. It was found that the sensor was sensitive to applied pressure and the response recovered back when the pressure removed. An annealed pressure sensor demonstrates better sensitivity and repeatability compared to un-annealed. The results indicated that the sensor performance was affected by the structure of the film. A crystalline structure gives an optimum response towards pneumatic pressure. The correlation between annealing process with structure of SBBT and piezoelectric property will be discussed.

INTRODUCTION

Pressure sensors are one of the most common micro-sensors devices used in various industrial such as automotive, medical, military, aeronautical, hydraulics, instrumentation, process and industrial control [1]. Among the pressure or stress sensing materials, piezoelectric material is famous to be used because of the special capabilities such as fast response, ruggedness, high stiffness, ability to measure the quasi-static pressure and good thermal stability. All these features are essential in the dynamic pressure measurement, which is very important in various industrial areas. At present, lead zirconate titanate (PZT) based ceramic is most widely applied in piezoelectric thin film sensor because of its large piezoelectric coefficient. However the evaporation of toxic lead during the fabrication of their ceramic causes an environmental problem. Therefore, there is an increasing interest of investigating lead free of piezoelectric materials to replace PZT based piezoelectric ceramics.

Strontium Barium Bismuth Titanate $Sr_{1-x}Ba_xBi_4Ti_4O_{15.}$ (SBBT) is chosen as the pressure sensing material. It is a kind of lead free perovskite-type piezoelectric with a relatively high Curie temperature (T_c= 520°C), good piezoelectricity and thermal stability [2]. SBBT is one of the family called Aurivillius phase generally formulated as $Bi_4A_{m-1}B_mO_{3m-1}$. Their crystal structure can be regarded as a regular intergrowth of $(Bi_2\ O_2)^{2+}$ layers and $(A_{m-1}B_mO_{3m-1})^{-2}$ perovskite where A can be a mono, di or trivalent element allowing dodecahedral coordination, B is a transition element suited to octahedral coordination and m is an integer which represents the number of perovskite [3].
The deposition method to obtain SBBT thin film included sol gel technique, metal organic, chemical vapor deposition, RF magnetron sputtering [4] and laser ablation [5]. Sol gel offers an economical technique, able to obtain homogeneous films with large area, excellent composition control, low processing cost and high purity. Therefore, sol gel technique is widely acknowledged to be advantageous over physical deposition techniques. When using sol-gel technique to prepare the ferroelectric thin film, an annealing step is require to promote crystallization of the SBBT materials. A crystalline structure will give an optimum response towards pneumatic pressure. Therefore, it may effectively improve the response of the sensing element. This paper reports the fabrication of SBBT thin films without annealed and annealed at 500°C as pressure sensor by using sol gel technique.

EXPERIMENTAL DETAILS

The solution of SBBT was prepared by sol gel technique. The source materials are bismuth acetate $Bi(CH_3COO)_2$, barium acetate $Bi(CH_3COO)_2$, strontium acetate $Sr(CH_3COO)_2$ and titanium butoxide $(Ti(OC_4H_9\ )_4)$. Initially, the powder of bismuth, barium and strontium were dissolved in acetic acid containing 20% volume of deionize water at room temperature. A clear and transparent solution is obtained. In order to improve the stability of the solution, 0.1 ml of ethanol amine was added to the solution with constant stirring. Finally the solution titanium (IV) was dropped wisely to the solution in a proper molar ratio with constant stirring at room temperature to form a clear and yellowish transparent solution. The flowchart of the whole synthesis process of precursor solution is shown in Figure 1.

The prepared SBBT solution was ready to be used for spin coating. The SBBT films were spin coated on silicon wafer at 400 rpm for 30 second followed by heating process at 300°C in air for 15 minutes. The purpose of heating process is to evaporate the organic solvents. For annealing, the sample was heat treat in air at 500°C for 2 minutes.
The microstructures of the films have been studied to investigate the effect of annealing and properties of the films. The crystal structure of the SBBT thin film is examined using an X-ray diffractometer (XRD) (Cu Kα radiation). Dielectric measurements carried out using Solarton-Schlumberger impedance spectroscopy. Atomic force microscope, (AFM) is used to measure the roughness of the surface film. The thickness for single layer of SBBT thin film was measured by the elipsometer, Rudolf Model

Auto E1-111. For the homogeneities and grains size, its have been characterized by Scanning Electron Microscope (SEM).

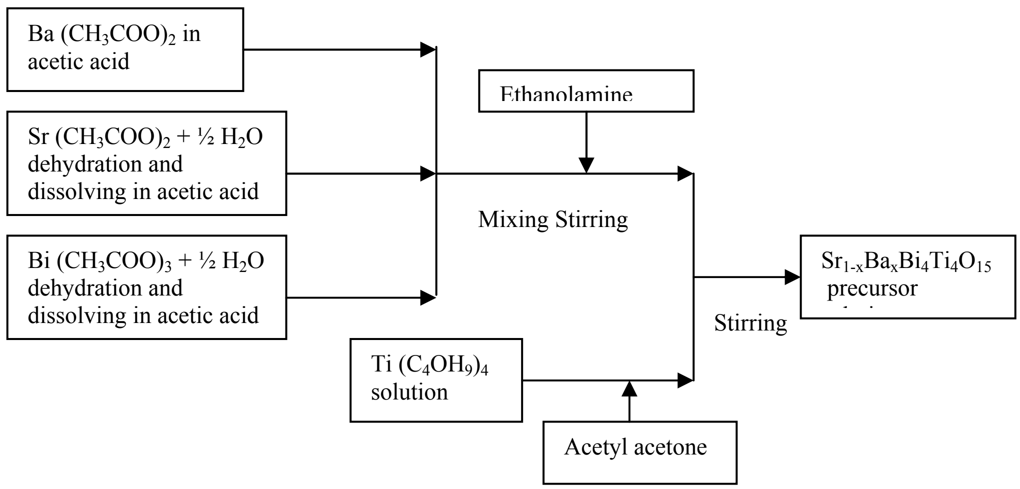


Figure 1: Flow chart of the fabrication process of SBBT.

The SBBT pressure sensors were fabricated with the structure of $Al/TiO_2/SBBT/TiO_2/SiO_2/Si$. The silicon oxides were deposited by electron beam evaporation with thickness of 1500 Å respectively. Ruthenium Oxide as bottom electrode was deposited by RF magnetron sputtering for 2 hours. In order to reduce the crystallization temperature for the formation of SBBT ferroelectric phase, the buffer layer, TiO_2 was then deposited on these films. Another purpose for the insertion of the buffer layer is to reduce hole injection layer and avoid the inter diffusion between film and electrode. The SBBT thin films were deposited on TiO_2/ RuO_2/ SiO_2/Si substrate followed by heat treatment at 300^0C. These spin coating and heating process was repeated five times to produce multilayer thin films. For annealing, the sample was heat treat in air at 500 ^{0}C for 2 minutes. To complete the fabricating of the pressure sensor, Al was deposited as a top electrode. The structure of the fabricated SBBT thin film pressure sensor is shown in Fig. 2.

The piezoelectric response of the sensor was measured using pneumatic loading method as shown in fig. 3. This measurement system has been divided into three parts: an air compressor system, pressure vessel and electrometer as data storage system. The pressure measurement was made from 0 to 450 kPa at room temperature. The air was compressed by the air compressor and imparted to the sensor, which was mounted inside the pressure vessel. The voltage that was generated by the sensor was collected by the electrometer.

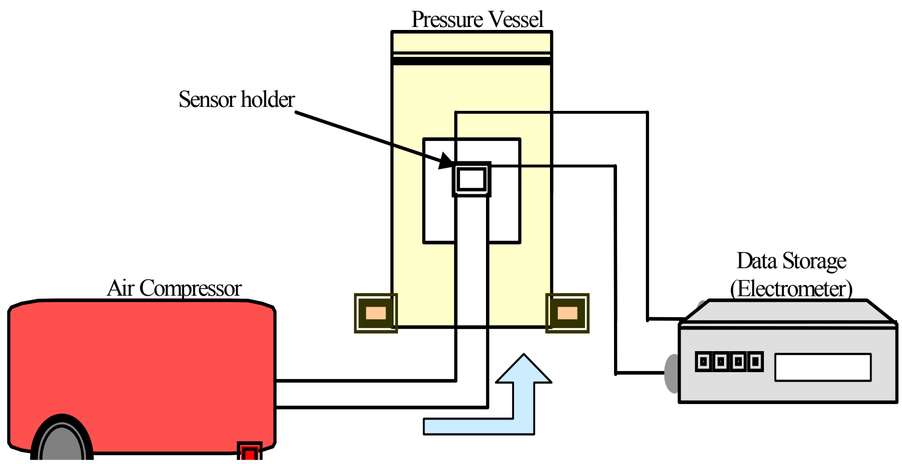


Figure 2: The fabricated SBBT pressure sensor.

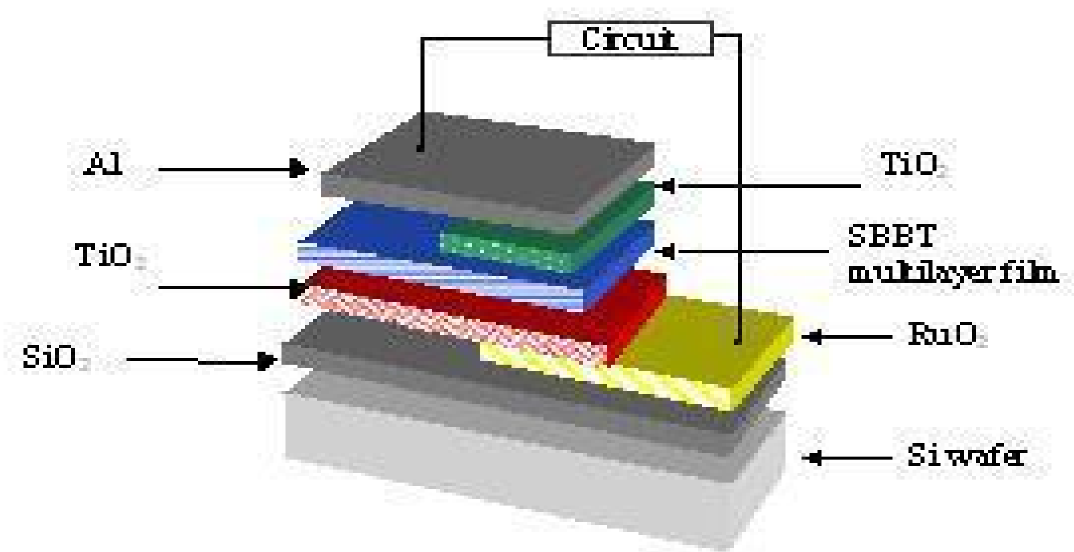


Figure 3: The measurement system of piezoelectric response.

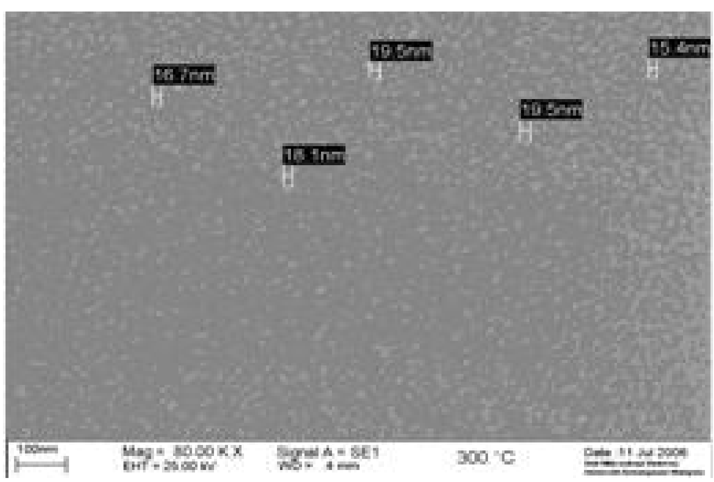
RESULTS AND DISCUSSION

Thin Films Characterization

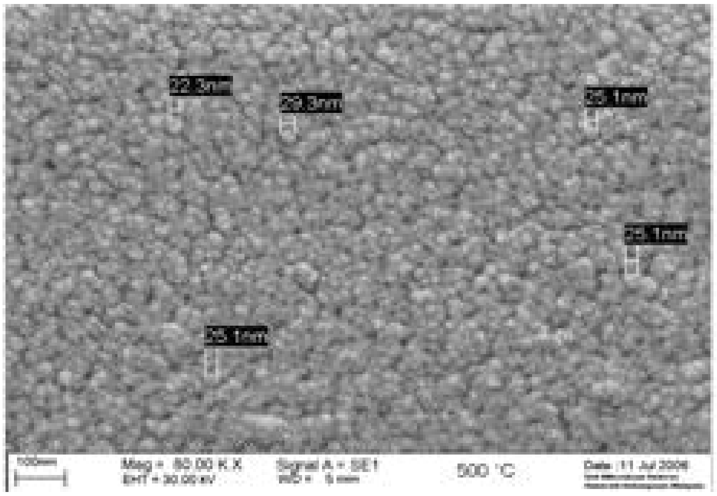
Figure 4 shows the SEM images of the surface morphology of SBBT thin films. The image indicated that an annealed film was in orderly forms, where the nano grains were formed with the clear grain boundaries. This feature is very important, since the electromechanical responds can be arose from the orderly oriented grains. The non annealed film grain size obtained in the range of 15.4 to 19.5 nm and the annealed film grain size obtains in the range of 22.3 to 29.3 nm. The grains size of SBBT films was increased after annealing. It means that the films exhibited a pronounced grain growth. This is reasonable since the coalescence of particles that caused by thermal effect. The average grain size and film thickness are presented in table 1.

AFM images are illustrated in Figure 5 and the surface roughness, R_a was calculated from the AFM images that shown in Table 1. The value of R_a indicated the surface morphologies of SBBT thin film are influence by annealing process. The annealed film tends to be smooth, thin and flat although the grains size as shown by SEM image is increased.

Fig 6 showed the XRD pattern of the SBBT thin film before and after annealing. It was found that the un-annealed film is in amorphous phase and it began to converse to crystalline phase after annealed at 500 ^{0}C. The annealed SBBT film indicated the co-existence of two phase $BaBi_4Ti_4O_{15}$ and $SrBi_4Ti_4O_{15}$, where the peak at (100) and (101) indicating the perovskite peaks with random crystalline orientation.
The dielectric properties of SBBT thin film measured in terms of the dielectric constant. The value of the dielectric constant was calculated from the capacitance of the film, measured at 1 kHz at an oscillation level of 20mV. The dielectric constant of un-anneal SBBT film is 72.81 and it found to be increase to 178.52 for SBBT film annealed at 500 ^{0}C. The higher dielectric constant is due to the better crystallite of the thin film after annealing process.



(a)



(b)

Figure 4: SEM photo of surface morphology of SBBT thin film (a) un-anneal and (b) anneal at 500^0C temperature

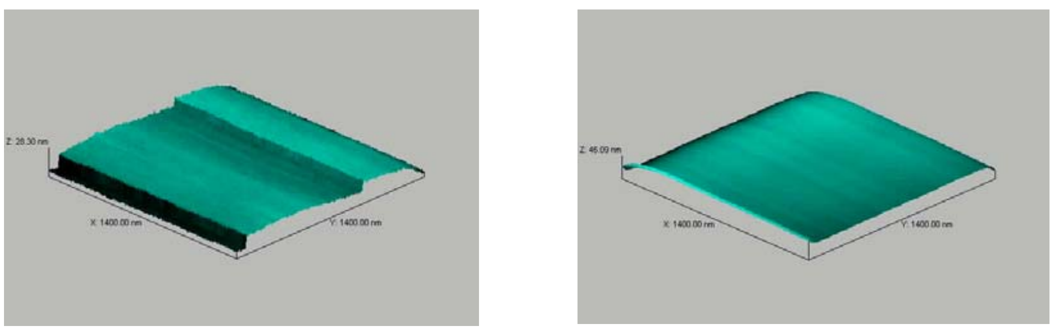


Figure 5: AFM images of the SBBT thin films (a) un-annealed and (b) annealed at 500^oC.

Measurements of piezoelectric response

The piezoelectric measurement system was designed using the concept of direct piezoelectric effect. When pressure is applied to piezoelectric materials, they create a strain or deformation in the materials, due to the deflection of the lattice in a naturally piezoelectric quartz crystal[6].

Figure 7 shows the piezoelectric response of the SBBT thin film sensors measured at pressure range from 0 to 450 kPa at room temperature. It is showed that the sensors were sensitive to the applied pressure and the responses were recovered back when the pressure is removed. The measurements were made for seven cycles at pressure 450 kPa. The sensors give responds to the applied pressure. An annealed pressure sensor showed better repeatability since the similar respond maintained until the seventh cycles.

The SBBT pressure sensor achieved a linear characteristic response between 50 kPa to 450 kPa pressure load. It was shown in Figure 8. The sensitivity of the sensors is represented by the slope of the graph and the R^2 is correlation coefficient. The graph demonstrates that an un-annealing sensor annealing process improve the sensing sensitivity.

It was found that the performance of the pressure sensors could be influenced by internal structure of SBBT thin films. Meanwhile the structure of the SBBT films is supposedly amorphous and the film was crystallized in perovskite phase after annealing at 500^{o}C. This structure is applicable for better electromechanical responds in the ferroelectric materials. The small dielectric constant for un-annealed sensor gave low capacitance that would present poor repeatability during continuous expossion at high piezo-voltage measurement, hence the voltage reduction or current leakage.

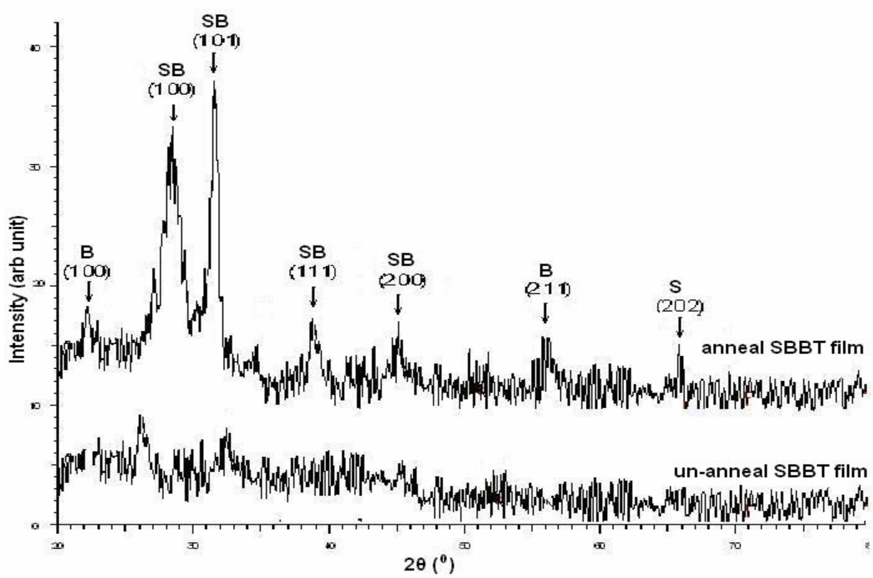


Figure 6: XRD patterns of $Sr_{0.5}Ba_{0.5}Bi_4Ti_4O_{15}$ thin films for un-annealed and annealed at 500^{o}C (S denotes $SrBi_4Ti_4O_{15}$ phase and B denotes $BaBi_4Ti_4O_{15}$ phase).

Table 1: Summarization of the annealed and non-annealed SBBT thin films on the dielectric property, surface roughness, thickness and grain size.

Annealing temperature (^{0}C)	Dielectric constant, ε	Roughness, Ra (± 0.01 nm)	Thickness, d (± 0.1 nm)	Average grains size (± 0.1 nm)
SBBT-0	72.81	10.48	92.3	17.84
500	178.52	4.15	143.6	25.38

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Based on the SEM result, it is suggests that nanostructure of the films would play important role to generate the high voltage and stable electromechanical response. When the grain size increase, the domain that carrying the dipoles will be increase as well [7,8]. In this kind of situation, the domains might have chances to be aligned in the preferential direction. The preferential oriented grains may become the active source for the piezoelectricity and generate great differential in electromechanical response, hence perform better sensitivity.

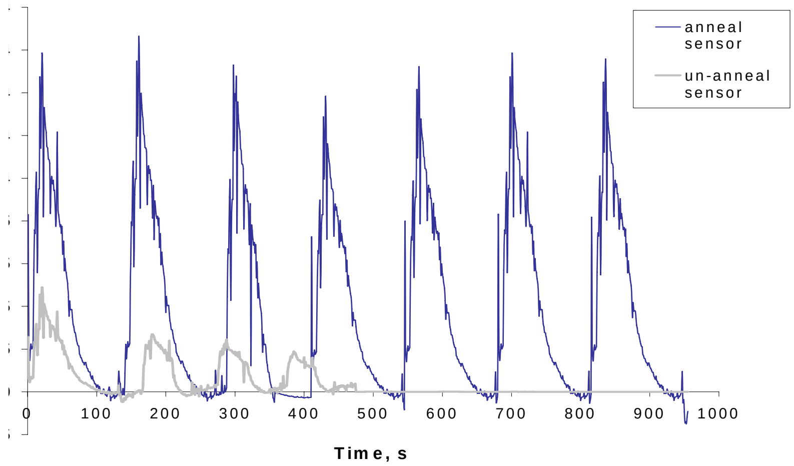
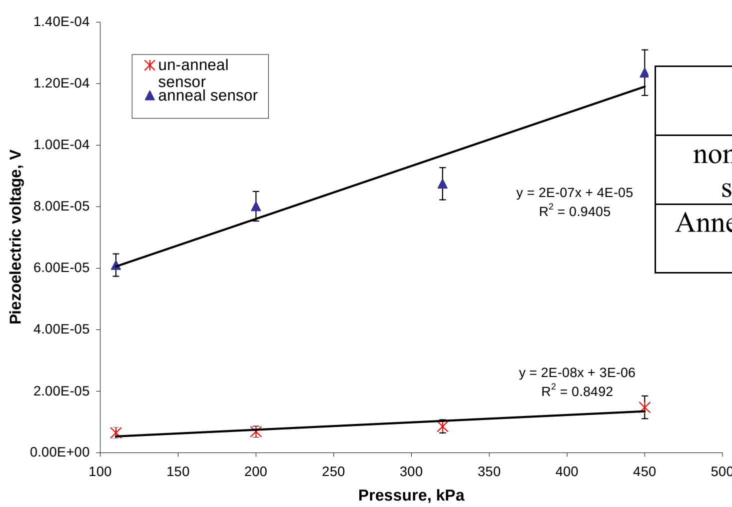


Figure 7: Voltage response of the SBBT thin films pressure sensor measures at pressure 450 kPa for seven cycles.



	Sensitivity µV/kPa
non-anneal sensor	0.02
Anneal sensor	0.2

Figure 8: Linearity of anneal and non-anneal SBBT pressure sensor. The sensitivity is calculated from the slope of the linearity graph.

CONCLUSION

The microstructure and piezoelectric responds of SBBT thin films pressure sensors have been systematically studied in as-prepared (un-annealed) condition as well as after annealing at 500^0C. The XRD results indicated that the SBBT film starts to converse from amorphous phase to crystalline after annealing at 500^oC. The dielectric constant and grain size were found toward higher value after annealing. The sensitivity of the sensors toward applied pressure was tested by pneumatic loading method. Both sensors give responds to the applied pressure. The performances of the devices influence by an annealing process. The annealed sensor is more sensitive and shows better repeatability. It can conclude that the performance of SBBT thin films pressure sensors were affected by the microstructure properties of the film.

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