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*Research Article*

# Effects of Deposition Temperature on Structural, Optical Properties and Laser Damage of $LaTiO_3$ Thin Films

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$LaTiO_3$ films were prepared under various deposition temperatures using electron beam evaporation on Si and fused quartz substrates. The relationship between the deposition temperature and structure and properties of optics was investigated by XPS, XRD, and various optical testing. The results showed that the $LaTiO_3$ film is amorphous when the deposition temperature is below 200°C. The refractive index of $LaTiO_3$ films increases from 1.8302 to 1.9112 at 1064 nm with the rise of deposition temperature. The extinction coefficient of $LaTiO_3$ films is less than $10^{-6}$ in the range of 350 to 1700 nm. The laser damage threshold increases at first and then decreases with the increase of deposition temperature. The maximum of the laser damage threshold was 18.18 J/cm$^2$ when the deposition temperature was 150°C. Compared with $TiO_2$ film, the chemical structure and the laser damage threshold of $LaTiO_3$ film are more stable by preparation of electron beam evaporation.

## 1. Introduction

Thin films began to be applied in the 1930s, and now it has been widely used in optics, microelectronics, materials, and other fields. However, with the application of high-power laser, the optical thin film which is an important part of the optical system has become a weak segment. For decades, the researchers have done a lot of work on improving the damage threshold of the thin film in optics field. For high refractive index materials, researchers focused on $HfO_2$, $TiO_2$, $ZrO_2$, and so on [1–5].

In recent years, with the discovery of high-temperature superconductivity and the development of its physical mechanism, the physical properties of $LaTiO_3$ due to the strong correlation of La-Ti-O doped with Ag, Cu, Fe, or Sr were extensively researched [6–9]. Meanwhile, the studies indicated that the performance of $TiO_2$ would be improved by $La_2O_3$ doped and obtained a high stability refractive index material—$LaTiO_3$ [10, 11]. Based on that, Philippe Combette studied the morphology, structure, nonconductivity, and dielectric properties of $LaTiO_3$ films under different deposition parameters (RF power, deposition pressure, and deposition temperature) [12]. Su Junhong studied the effect of deposition temperature on optical properties and laser damage characteristics of $LaTiO_3$ films [13]. However, few studies have made a systematic study on the relationship between structure and optical properties of $LaTiO_3$ thin films.

As we know, the preparing parameters have an important effect on the properties of the film [14, 15]. Therefore, the effects of deposition temperature on the optical and the laser damage properties of $LaTiO_3$ thin films were studied in this paper.

## 2. Experimental

$LaTiO_3$ films were deposited by electron beam evaporation (ZZS500-1/G Chengdu Nanguang Vacuum Technology Co. Ltd., China) on Si (100) and fused quartz substrates. The films were deposited by using the $LaTiO_3$ pellets (purity 99.99%, provided by Beijing Nonferrous Metal Research Institute) as starting material. Si (100) and fused quartz substrates were cleaned ultrasonically in alcohol solution before deposition. The base pressure was $3 \times 10^{-3}$ Pa and the working pressure was $2 \times 10^{-2}$ Pa, oxygen was introduced in the vacuum

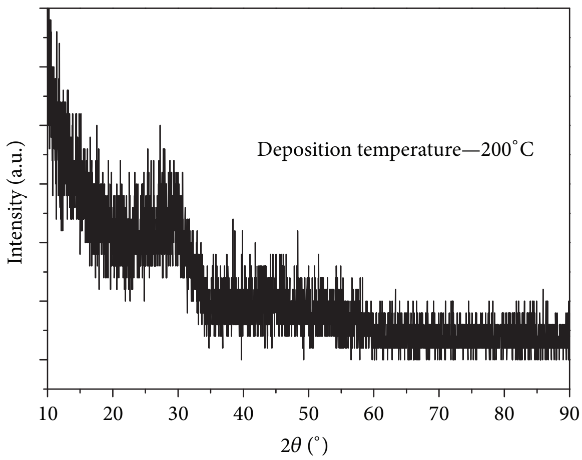



Figure 1: XRD spectra of sample deposited at 200°C.

chamber and the gas flow was kept at 4 sccm, the electron beam current was 110 mA, and the deposition temperature, respectively, was 50, 75, 100, 125, 150, 175, and 200°C.

Optical parameters of the $LaTiO_3$ films, including refractive indexes, extinction coefficient, and physical thickness, were measured by spectroscopic ellipsometry (J.A. Woollam M-2000UI, American). The structure of the samples was measured by X-ray diffraction (XRD, X'Pert PRO MPD) with $2\theta$ angle in the range of 10–90° at room temperature. The transmission spectra of the films were measured by spectrophotometer (HitachiU-3501, Japan). The elemental composition and the element's chemical states of the as-deposited $LaTiO_3$ films were investigated by X-ray photoelectron spectroscopy (XPS, PHI5400). Laser damage characteristics of $LaTiO_3$ films were measured by the film and optical element laser damage threshold testing instrument. The laser induced damage threshold (LIDT) of thin films was measured in "1-on-1" regime according to ISO standard 11254-1 by means of 1064 nm $Q$-switch pulsed laser with a pulse length of 10 ns.

## 3. Result and Discussion

*3.1. Different Deposition Temperature*

*3.1.1. X-Ray Diffraction Analysis.* The XRD spectra shown in Figure 1 revealed that no apparent diffraction peak can be found but an amorphous package around $2\theta = 28°$. It means that the film even deposited at the highest temperature of 200°C is still amorphous.

*3.1.2. XPS Spectrum Analysis.* Figure 2 shows the XPS characteristic spectra of La, Ti, O, and contamination C, which were detected in the XPS survey spectra of the film prepared at 125°C. The peak of Ti2p3 of 457.97 eV in Figure 2 was close to the value of 457.80 eV in $Ti_2O_3$ [16]. The peak of La3d5 was 834.12 eV corresponding to 834.80 eV of $La_2O_3$ [17]. It indicated that the film was essentially composed of $La_2O_3$ and $Ti_2O_3$. The XPS results of films deposited at different temperatures are listed in Table 1. It showed that the ratio of total La and Ti atomic content to O atomic content was approximated to 2 : 3 and increased slightly with the increase of deposition temperature. It indicates that the increase of deposition temperature benefited the formation of $LaTiO_3$. Meanwhile, the change of the ratio was not obvious, indicating that the evaporation is stability.

*3.1.3. Optical Properties.* Optical properties can be characterized by refractive index and transmittance which are important parameters for optical applications [18]. The results of optical constants $n$ and $k$ of $LaTiO_3$ films were shown in Figure 3. As shown in Figure 3(a), the refractive index increases with the rise of the deposition temperature in the wavelength range from 350 to 1700 nm. From the analysis of XPS results, it has been known that the difference in composition of the film is small. Therefore, the increase in refractive index could be the major mobility of the film atoms on the substrate at higher deposition temperatures, which would help to achieve high aggregation densities and lead to the increase in the refractive index. Simultaneously, Figure 3(a) showed that the refractive index increased from 1.8302 to 1.9112 at the wavelength of 1064 nm with a small variation of 0.081. However, some studies have shown that the refractive index of $TiO_2$ films dramatically increases from 1.8458 to 2.0721 when the substrate temperature increased from 50 to 250°C [19]. The variation is as high as 0.2263. Consequently, the refractive index change of $LaTiO_3$ films is much smaller than that of $TiO_2$ film with the same change of deposition temperature. In other words, $LaTiO_3$ film is better than $TiO_2$ film in structural stability at different deposition temperatures. In addition, some researcher concluded that the refractive index of $TiO_2$ film deposited by electron beam evaporation at 200°C is 2.07–1.95 in the wavelength of 400–900 nm, while the refractive index of $LaTiO_3$ film is 2.04–1.93 under the same conditions. Obviously, the refractive index of $LaTiO_3$ film is almost equal to that of $TiO_2$ film. From Figure 3(b), it can be seen that the extinction coefficient of all samples is less than $10^{-6}$ in the wavelength range of 350 to 1700 nm, which showed that the absorption of the film was smaller.

The transmission spectra of samples at different deposition temperatures were shown in Figure 4. With the exception of the transmittance less than 80% at range of 424–480 nm due to optical interference, it can be observed that the transmittance of all samples are greater than 80% at wavelengths over 330 nm. The transmittance curves of 500–700 nm wavelength range were shown in Figure 4. As shown, the higher the deposition temperature, the closer the maximum transmittance of the $LaTiO_3$ film and the substrate transmittance. At the wavelength of 592 nm, the highest transmittance 93.44% occurs in the 200°C deposited film, which is very close to the substrate transmittance of 93.47%. Coinciding with extinction coefficient curve, the results of transmittance indicated $LaTiO_3$ films could be used as excellent transparent layers.

*3.1.4. Laser Damage Property.* In general, multilayer optical coatings were prepared by alternative depositing high and low

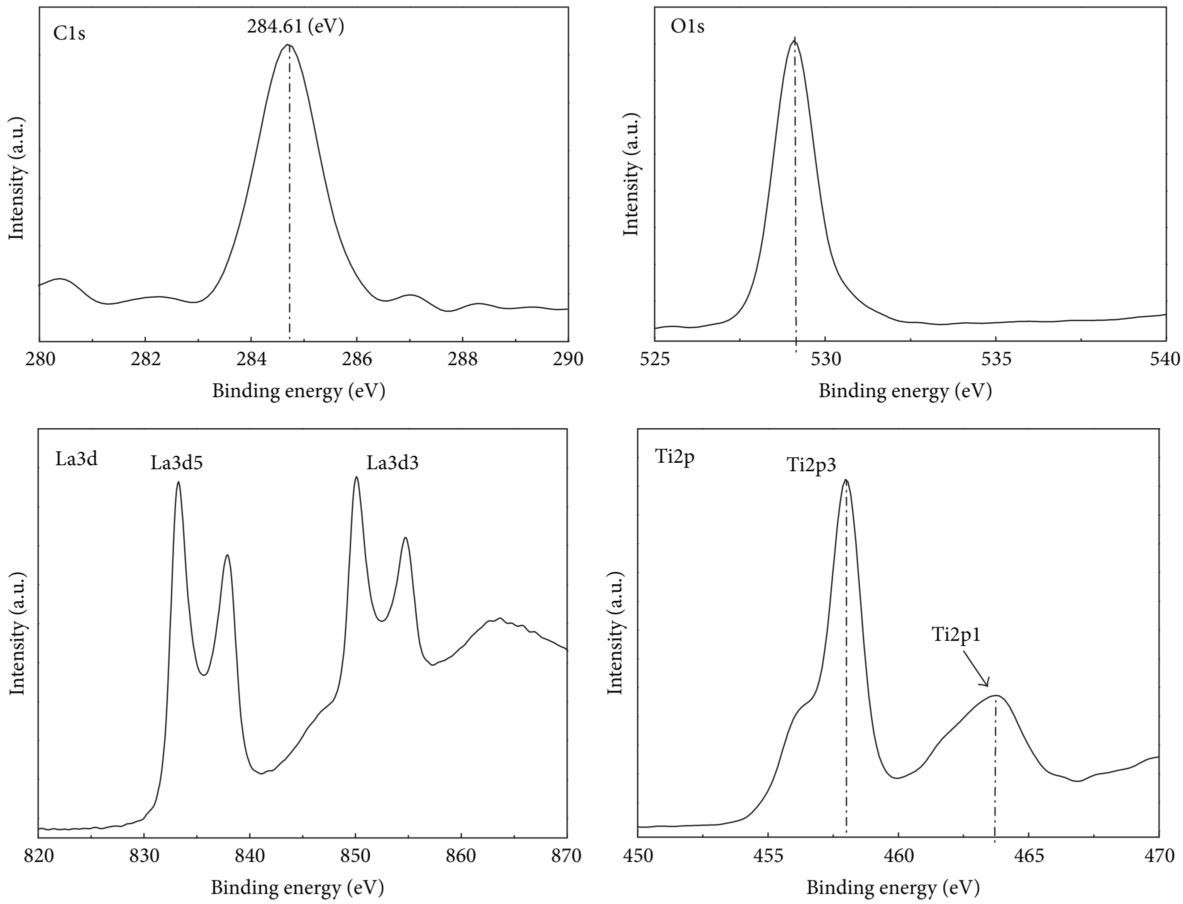



FIGURE 2: XPS spectra of four elements La, Ti, O, and C.

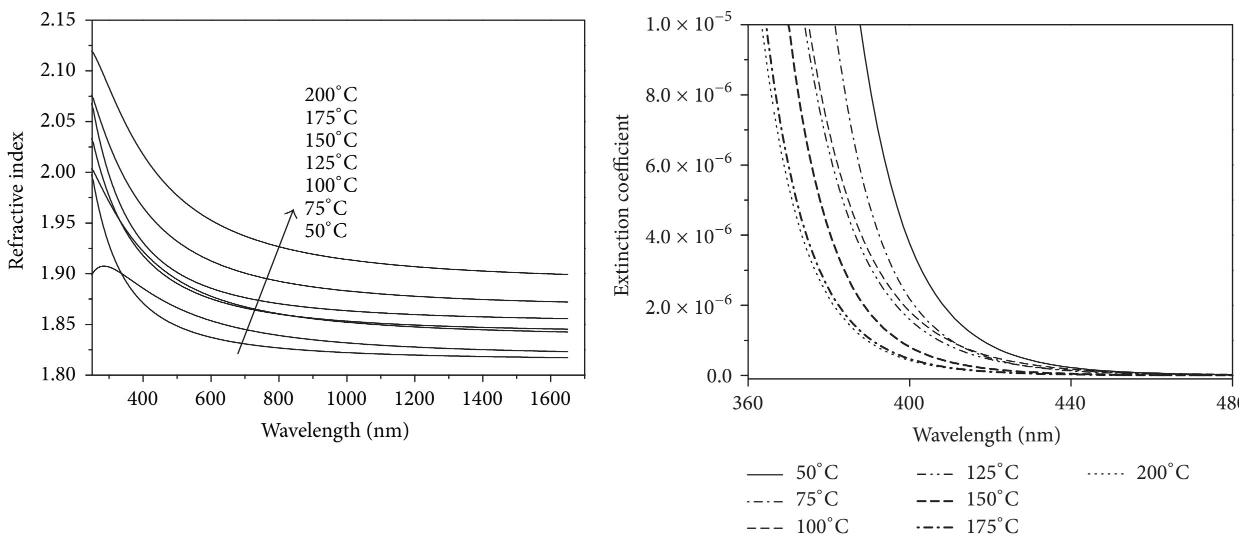
TABLE 1: Content of elements in the films prepared at different deposition temperature.

| Deposition temperature | At (%) | | | | |
|---|---|---|---|---|---|
| | C1s | La3d | O1s | Ti2p | (La3d + Ti2p): O1s |
| 50 | 6.01 | 22.42 | 58.29 | 13.28 | 0.6125 |
| 75 | 5.79 | 22.27 | 58.82 | 13.12 | 0.6017 |
| 100 | 4.32 | 22.61 | 59.85 | 13.22 | 0.5987 |
| 125 | 4.58 | 22.87 | 59.36 | 13.19 | 0.6075 |
| 150 | 2.46 | 23.30 | 60.74 | 13.50 | 0.6059 |
| 175 | 2.98 | 23.53 | 60.00 | 13.49 | 0.6170 |
| 200 | 3.65 | 23.83 | 58.88 | 13.64 | 0.6364 |

refractive index materials. The high refractive index materials were metal oxide material mostly, which were prone to lose oxygen during deposition process and became a shortcoming of multilayer film in the field of laser damage. Therefore, it was necessary to study the laser damage properties of $LaTiO_3$ films.

The surface damage morphologies of $LaTiO_3$ films prepared at 50, 150, and 200°C have been presented in Figure 5. This group of experiments was performed at 180 mJ pulsed laser energy. The damage performance of films deposited at different temperatures was directly analyzed from the damage spot area. As shown in Figure 5, all the samples were damaged. Among them, the shedding area on the surface of the film deposited at 50°C was the largest one, which indicated the film damage was the most serious. When the deposition temperature was from 150 to 200°C, the shedding area was increased slightly. However, in general, there is no significant difference in damage morphologies of the films prepared at different deposition temperatures.

The LIDT of different deposition temperatures were shown in Figure 6. The LIDT increased with the rise of deposition temperature from 50 to 150°C. The maximum value of LIDT was 18.18 J/cm$^2$ at 150°C. However, the LIDT start to decrease when the deposition temperature was higher




(a) Refractive index

(b) Extinction coefficient

FIGURE 3: Refractive index (a) and extinction coefficient (b) of samples.

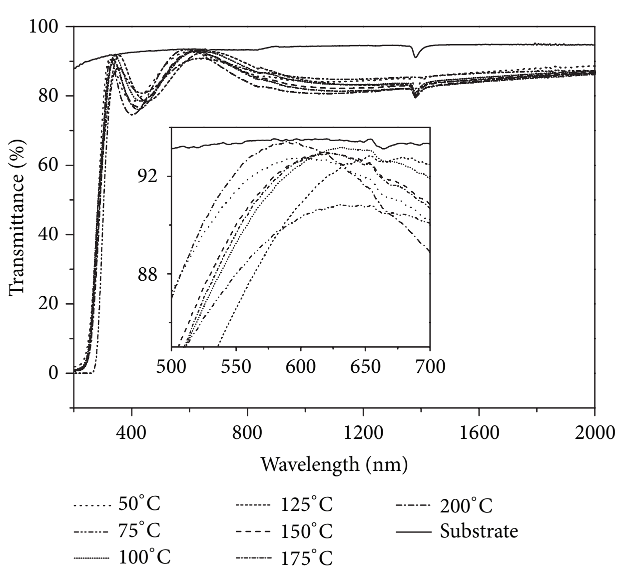



FIGURE 4: Transmittance curve of the films prepared at different deposition temperatures.

than 150°C. The LIDT of the 200°C deposited film closing to 15.91 J/cm$^2$ of the 50°C one reaches to 15.78 J/cm$^2$. It can be seen that the LIDT of the film did not change monotonically with the increase of deposition temperature and it was the maximum at 150°C.

In combination with XPS analysis, it was found that composition of the film prepared at different temperatures changed slightly so as to have little effect on the LIDT. Therefore, the depositing temperature became the main factor to affect the laser damage property. It concludes that the higher LIDT can be obtained at the higher depositing temperature. Firstly, at the higher deposition temperature the film had higher concentration density and thermal capacity than that at the lower deposition temperature. Secondly, the higher deposition temperature not only improved the hardness of the films but also enhanced the adhesion between film and substrate. These results dramatically improved the film against the rapid heat expansion when the high energy laser propagated in the film. Finally, the higher deposition temperatures make the atoms of the film to gain more kinetic energy, which would increase the atomic migration velocity and reduce the defects of the film. However, the higher temperature also leads to an increasing internal stress of film, which can be observed from the crack around damage boundary of the film prepared at 200°C and results in the decrease in LIDT.

Compared with the $TiO_2$ film [20], the LIDT of $LaTiO_3$ film is about 15.78–18.18 J/cm$^2$, which is higher than that of $TiO_2$ film deposited at 200°C about 4.2 J/cm$^2$.

## 4. Conclusion

The deposition parameters have important effects on the performance of the film. The deposition temperature effects on structural and optical properties and laser damage of $LaTiO_3$ thin films were studied in this paper. The results show that the refractive index of $LaTiO_3$ film increased with substrate temperature. The extinction coefficient was less than $10^{-6}$ in the wavelength range of 350 to 1700 nm, which shows that the absorption of $LaTiO_3$ film is very small. It can be used as an ideal optical coating material. The LIDT increases at first and then decreases with increase of deposition temperature, and the maximum is 18.18 J/cm$^2$ at the deposition temperature of 150°C and is higher than $TiO_2$ film. But all the differences of performance were small and were insensitive to deposition temperature. Overall, process stability of the $LaTiO_3$ film is better than those of $TiO_2$ film. The $LaTiO_3$ film is an excellent optical coating and laser protection material.


Figure 5: Damage morphologies of $LaTiO_3$ film prepared at different deposition temperature.

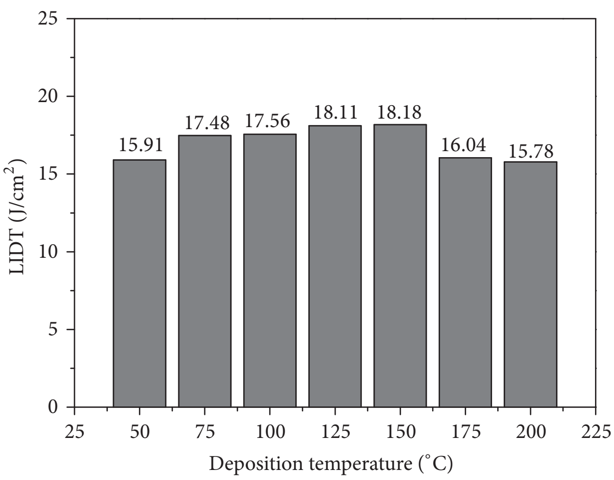



Figure 6: LIDT of $LaTiO_3$ film prepared at different deposition temperatures.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

## Acknowledgments

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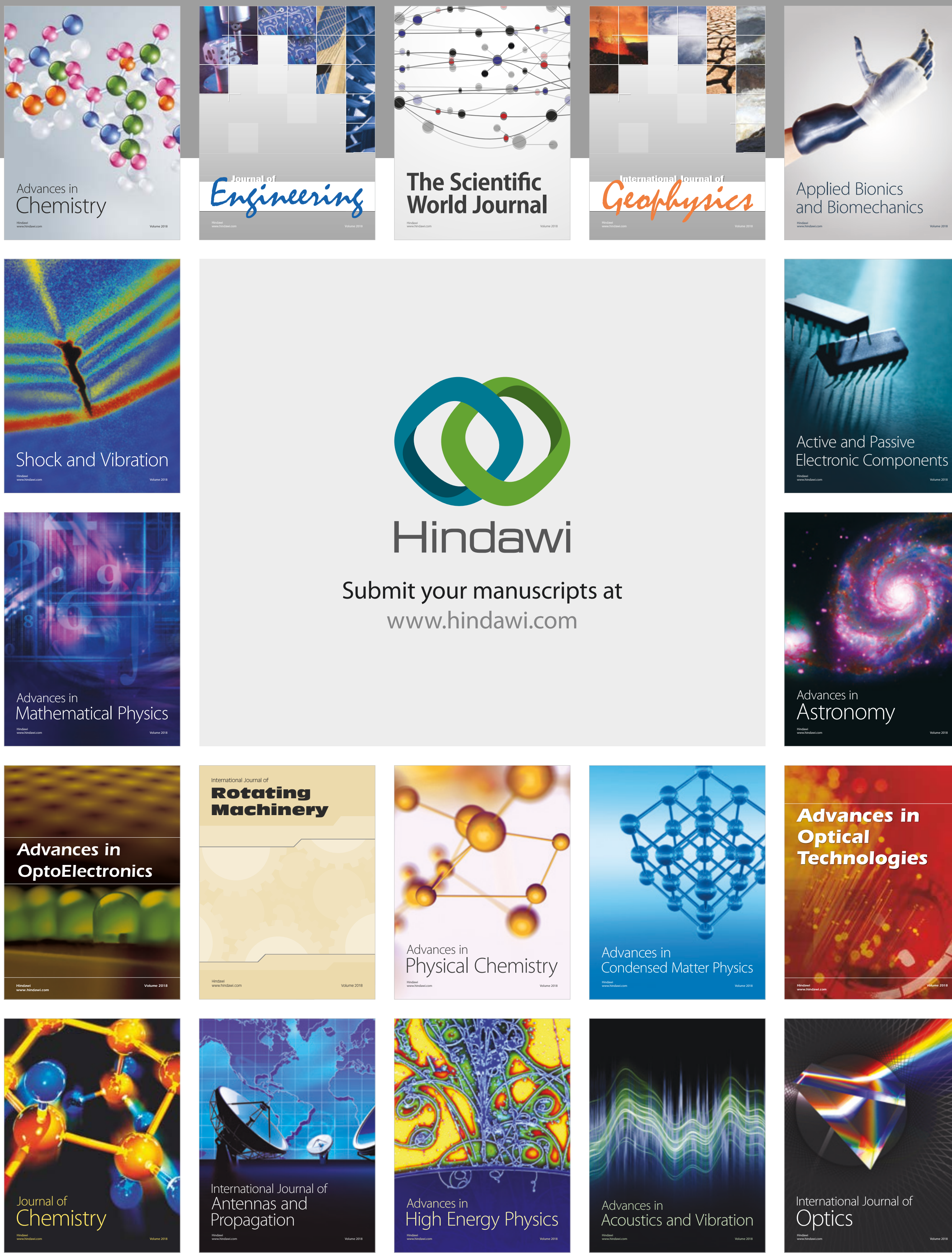
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