Radio Frequency Plasma-Enhanced Reactive Magnetron Sputtering Deposition of $\alpha$-SiN$_x$ on Photonic Crystal—Laser Diodes for Facet Passivation

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ABSTRACT: Amorphous silicon nitride ($\alpha$-SiN$_x$) films were coated on a photonic crystal-laser diode by the radio frequency magnetron sputtering method. Sputtering deposition conditions were changed to obtain $\alpha$-SiN$_x$ films with different properties. The optical parameters and morphologies of the products were systematically characterized by spectroscopic ellipsometry fitting, energy-dispersive X-ray spectroscopy, atomic force microscopy, and performance of LDs coated with $\alpha$-SiN$_x$ films were tested at 25 °C. Physical mechanisms of sputtering were explained in detail. $\alpha$-SiN$_x$ with a band gap of 4.4 eV and a refractive index of 2.03 at 980 nm were grown. The extinction coefficient equal to 0 at 980 nm, and the surface morphology tended to be homogeneous and dense. The main influencing factors related to the catastrophic optical mirror damage (COMD) phenomenon were investigated. Then plasma pretreatment was implemented to eliminate defects and improve the cavity surface quality and further optimized by measuring the intensity of photoluminescence. Afterward, a rapid annealing method was also carried out to improve coating performance. Finally, $\alpha$-SiN$_x$ acted as a passivation layer in the antireflection film coated on the LD facets and the COMD threshold increased from 5 to 15.2 W, which led to a higher reliability than nonoptimized LDs and elimination of the COMD phenomenon.

1. INTRODUCTION

Catastrophic optical mirror damage (COMD) is an important factor that limits the maximum output of high-power semiconductor laser diodes (LDs) and endangers the safety of the LD system. For GaAs-based LDs, when its natural cleavage surface is exposed to air, is easily oxidized to form Ga$_2$O$_3$ and As$_2$O$_3$. These oxides become nonradiative recombination centers and generate many surface energy levels. Especially when the semiconductor LD works at a high power, these nonradiative recombination centers absorb photons, resulting in the huge generation of heat. Then the thermal effect causes bandgap shrinkage of the semiconductor materials in the LD facet, which accelerates surface material oxidation and generates more nonradiative recombination centers, further increasing the absorption of photons. There is a cyclical growth of light absorption, heat accumulation, and bandgap shrinking. Finally, COMD occurs when the surface temperature reaches the melting point and provokes thermal runaway, causing irreversible and permanent damage to the device.

At present, for the purpose of increasing the COMD threshold of LDs, the passivation film is usually coated on the semiconductor-cleaved surface to alleviate surface oxidation and guarantee the safety of the laser system. Silicon nitride is an excellent passivating material on account of its excellent properties such as wide bandgap (>4.0 eV), good moisture resistance, high thermal stability, and mechanical hardness, which attracted the attention of many researchers. As the passivation film, SiN$_x$ can increase the lifetime of the LD by 15 times than ZnSe and contains less Ga–O and As–O than Al$_2$O$_3$, which is expected to have a better passivation effect on the LD facet. It has been reported that AlN increased the power by 30% to 1.8 W$^{21}$, which need to be further improved. The COMD threshold of ZnSe coated on a 915 nm laser was 14.8 W.$^{22}$ In our group, Al$_2$O$_3$ was used as the passivation layer on the photonic crystal-LD (PC-LD), and the maximum continuous output power was 7.3 W.$^{23}$

Various techniques have been applied to grow passivation films on cleavage surfaces to prevent oxidation and improve the interface quality of LDs. Considering that atomic layer deposition technology needs complex equipment and the process temperature is over 500 °C, which may accelerate...
cavity surface oxidation and affect the lifetime of LDs. The wet sulfur-solution method takes a long time and has a poor stability in the passivation process. We put forward radio frequency (RF) magnetron sputtering as the passivation method, which is a cost- and time-effective technology and has a suitable film growth rate as well as convenient materials and equipment. In the past years, the optical properties of thin film materials and RF magnetron sputtering technology have been studied, and the porosity of silicon nitride thin films was controlled by changing the chamber temperature, gas mixing ratio, distance between the target and substrate, constant power supply voltage, and so on. Therefore, a systematic research of the relationship between properties of magnetron sputtering films and their performance on LDs is highly needed.

This paper focuses on the influence of RF magnetron sputtering deposition conditions on the properties of amorphous silicon nitride (α-SiNₓ) thin films, establishing a correlation between the optical properties of α-SiNₓ and the COMD phenomenon of LDs. In the end, the optical power of LDs coated with α-SiNₓ increased by more than three times than that of uncoated LDs.

2. RESULTS AND DISCUSSION

As shown in Figure 2, the refractive index of the SiNₓ film increases from 1.84 to 2.04 at a wavelength of 980 nm with different electron gun power from 1200 to 1500 W. Because increasing the electron gun power will sputter out more silicon atoms, and the film will be developed toward the Si-rich SiNₓ film and cause the increase of the refractive index. However, the refractive index of the film declined to 1.98 at 980 nm when the electron gun power increased to 1600 W. This is due to the fact that excess silicon atoms sputtered out can increase the vacancy of the N atom in the lattice, which will reduce the structural compactness of the film. The extinction coefficient k of the five samples varying with different sputtering power in the photon energy range from 0.75 to 5 eV is shown in Figure 3. It is clear that k increases monotonically with the increase of the sputtering power under the same photon energy. k and the sputtering power are (10, 1200 W), (260, 1300 W), (300, 1400 W), (320, 1500 W), (350, 1600 W), respectively, when the photon energy E is 1.24 eV (980 nm lasing wavelength). Because with the increase of the sputtering power, the sputtered silicon atoms are deposited on the substrate without sufficient diffusion, making the film to grow like an island. Therefore, there are many defects on the surface of the film, which become the auger recombination capable of absorbing photons. Figure 4 shows that k increases with the sputtering power in the range of 1200–1600 W. At the same time, E_g decreases with the sputtering power increasing, which can conclude that α-SiNₓ begins to change from the nitrogen-rich type into silicon-rich type. This change may introduce impurities of uncombined silicon atoms, eventually becoming nonradiative recombination centers. This opinion can also be proved in Figure 5, the power of the electron gun is 1600 W, silicon atoms account for 45% of the total number of nitrogen and silicon atoms. When the power of the electron gun is 1400 W, silicon atoms account for 37% of the total number of nitrogen and silicon atoms. When the power of the electron gun is 1000 W, silicon atoms account for 31% of the total number of nitrogen and silicon atoms. Therefore, the power of the electron gun has an influence on the composition of the SiNₓ film.

The relationship between the refractive index n of SiNₓ films and the Ar flow rate were investigated, as shown in Figure 6a.
With the Ar flow rate increasing, the refractive index also increases at a wavelength range of 380–1650 nm. It is because the increase of Ar\textsuperscript{+} sputters out more silicon atoms, making the film a silicon-rich silicon nitride with a higher \( n \).

The influence of the Ar flow rate in sputtering ambient on the absorption coefficient of the prepared film is shown in Figure 6b. With the increase of the Ar flow rate, \( \alpha \) generally followed an increasing trend from 0.75 to 3.25 eV. In terms of 1.24 eV, as illustrated in Figure 6, \( \alpha \) is equal to (0 cm\(^{-1}\), 50 sccm), (10 cm\(^{-1}\), 60 sccm), (170 cm\(^{-1}\), 65 sccm), (420 cm\(^{-1}\), 70 sccm), and (500 cm\(^{-1}\), 75 sccm), respectively. Because the photon energy is far less than the bandgap of SiN\(_x\) (approximately 4 eV), the photon absorption is mainly caused by the excess Si atoms sputtered out, which have a lower bandgap (1.14 eV).

Figure 7 shows the influence of the N\(_2\) flow rate on the refractive index and \( \alpha \). The Ar flow rate of the electron gun is set as 50 sccm. In Figure 7a, \( n \) decreases with the N\(_2\) flow rate increasing, meaning the film packing density also decreases with the N\(_2\) flow rate. In Figure 7b, \( \alpha \) decreases with an...
increasing N₂ flow rate as well. The surface microstructures of the α-SiNₓ samples were observed by atomic force microscope (AFM), as shown in Figure 8. The size of the scanned area was 10 μm × 10 μm. The roughness reduced from 0.56 to 0.19 nm as the N₂ flow rate was increased from 8 to 16 sccm. Progressive homogeneous and densification of the film microstructure occurring as the N₂ flow rate was increased, which was consistent with previous report. The most smooth, flat surface was obtained when the N₂ flow rate was 16 sccm. From these results, we draw a conclusion that the sample with low roughness has a low absorption coefficient.

The influence of the RF power on the refractive index was investigated, as shown in Figure 9. Obviously, the n decreases with the increase of the RF power range from 400 to 500 W, and rise with the increase of the RF power range from 500 to 600 W. This can be divided into two steps: (1) Si atoms and N⁺ have been pushed by high-energy ions, enhancing the adhesion to the substrate and increasing the structural compactness of the SiNₓ film, so n increases; (2) when further increasing the RF power range from 500 to 600 W, the increase of the nitrogen ionization rate increases the opportunity for silicon atoms to combine with N⁺, so n decreases. Whether the refractive index increases or decreases mainly depends on which of the above two cases is dominant.

The influence of the chamber temperature on the refractive index of the SiNₓ film is shown in Figure 10. It is observed that the refractive index decreases with the increase of the chamber temperature from 25 to 80 °C. Because raising the temperature will provide the atoms more lateral diffusion energy, and then the atoms will become mobile and form new dimers. But further rising the temperature from 80 to 120 °C, the refractive index decreases. This is because of the collision between the silicon atoms is aggravated by the increase of temperature, which reduces the energy of the silicon atoms when they reach the substrate, and make the film loose.

3. APPLICATION ON LD DEVICES

3.1. Plasma Cleaning Process. Photoluminescence (PL) spectrum intensity can indicate the passivation efficiency to some extent. In order to investigate whether surface impurities and oxidation defects have been removed, three groups of the GaAs substrate bombarded with N₂, Ar, and mixed gas with 70% N₂ and 30% Ar were carried out, after that 30 nm α-SiNₓ films were grown on the substrates with the same growth conditions. The PL intensity of GaAs-coated α-SiNₓ with different cleaning gases are clearly shown in Figure 11. When the cleaning time was shorter than 7 min, the Ar cleaning group showed the lowest intensity, which dropped dramatically for a longer time (from 7 to 30 min). The intensity of the N₂ cleaning group was lower than the mixed gas cleaning group before 10 min, getting the highest intensity at 15 min. The mixed gas cleaning group got the highest intensity before 10 min and there was no significant reduction over 30 min. This was because the energy of the N plasma is lower than that of the Ar plasma, which caused no additional defects but a slower cleaning speed. Comparatively speaking, mixed plasma is suitable for surface cleaning with moderate
energy cleaning and less cleaning time. Therefore, it is advisable to pretreat the cavity surface with a mixture of N₂ and Ar.

3.2. Results of Laser Performance with α-SiNₓ as the LD Passivation Film. Four groups of GaAs-based PC-LDs with different growing conditions of SiNₓ were fabricated and measured. The LDs were all the same except the passivation film. The curves of LD output power versus current with different α are shown in Figure 12. It can be learned that when α was equal to 0, LDs reached the maximum power, 15.2 W at 16 A, and as the current increases after 16 A, thermal saturation occurred which resulted in the decline of the power. For LDs coated with SiNₓ with an α of 10 cm⁻¹, the maximum power dropped to 14 W and the slope efficiency of the curve decreased slightly. This is because the premature occurrence of thermal saturation caused by the increase of photon absorption. We can draw a conclusion that heat dissipation is a more important limiting factor than cavity coating. When α increased to 10² cm⁻¹, COD happened at 8 W, and the COD threshold decreased to 5 W as α added up to 5 × 10² cm⁻¹. The absorbed photons caused heat accumulation to reach the melting point of the cavity surface material. It can be concluded that α needs to be less than 10 cm⁻¹ to avoid COD that happened for 4 mm long and 90 μm wide high-power semiconductor LDs.

3.3. Annealing Effect on LDs Coated with a α-SiNₓ Thin Film. α-SiNₓ always contains a few silicon atomic clusters. To get high optical quality films with lower absorption losses, we used the rapid anneal method in a hydrogen chamber pressure (Pa)

Table 1. Deposition Conditions for SiNₓ Film Coating

| Parameter       | Value                        |
|-----------------|------------------------------|
| Target material | Si (99.99%), Ta (99.99%)     |
| Gas source      | N₂ (99.99%), Ar (99.99%), O₂ (99.99%) |
| Electron gun power (W) | 1200–1600                  |
| Bias voltage (V) | 400                          |
| Sample          | GaAs (100) oriented          |
| LD type         | PC-LD with 90 μm stripe width and 4 mm cavity length |

Table 2. Annealing Conditions for SiNₓ Film Coating

| Temperature (°C) | α (cm⁻¹) | Roughness (nm) | Average COD Threshold for five LDs (W) |
|------------------|----------|----------------|--------------------------------------|
| 250              | 24       | 0.54           | 10.2                                 |
| 300              | 15       | 0.58           | 10.7                                 |
| 350              | 16       | 0.56           | 7                                    |
| 400              | 15       | 0.56           | 5                                    |

Figure 12. Curves of power versus current for the SiNₓ film of four samples.

residual Si atoms, which reduces the hanging bond. Meanwhile, there was no significant change for roughness, which proved that the annealing process with these temperatures does not reconstruct the lattice.

However, on further elevating the temperature to more than 350 °C, the COD threshold decreased. The possible reason is that the oxygen molecules in air form chemical bonds with Ga and As in the LD facet when above 350 °C, and COD is easy to occur. Therefore, proper annealing conditions are critical for improving the stability of the laser film.

4. CONCLUSIONS

We introduced the method of RF plasma-enhanced reactive magnetron sputtering growing α-SiNₓ. The effects of the electron gun power, argon flow rate, nitrogen flow rate, ion source power, and film growth temperature on the refractive index, extinction coefficient, surface morphology, and element ratio of the α-SiNₓ film were investigated. It has been proved by experiments that the main factor leading to the difference of light absorption of the α-SiNₓ film is the change of the composition ratio of the film. In addition, we demonstrated a correlation between the COD phenomenon and parameters of the laser facet passivation film, and the performance of the products was improved by changing the magnetic conditions and further optimizing the coating effect with N₂/Ar-mixed plasma treatment and rapid annealing. The α-SiNₓ thin film with a bandgap of 4.4 eV and a refractive index of 2.03 at 980 nm were coated on the LD facet, and the extinction coefficient was equal to 0 at 980 nm, roughness was equal to 0.19 nm. Finally, the LD test result shows that the optimized film has a remarkable effect on the LD facet to prevent COD, which is greatly helpful for the stability of the laser system.

5. COMPUTATIONAL METHODS

The refractive index n(λ) and the extinction coefficient k(λ) in the wavelength range of 245–1650 nm can be extracted by spectroscopic ellipsometry fitting and analyzing by the Cauchy model

\[ n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \]

In some research the band tail absorption associated with impurities has been neglected. In order to characterize the weak absorption in almost transparent regions, in this paper k was calculated by using the Urbach equation

\[ k(\lambda) = A_k e^{(E-E_0)/\lambda} \]

The optical absorption coefficient (α) can be expressed by using

\[ \alpha = 4nk/\lambda \]

where \( \lambda \) is the wavelength.
The cavity surface absorption is mainly caused by auger recombination, and the electron transition is indirect. \( \alpha \) caused by the electron transition can be expressed as

\[
\alpha = B(h\theta - E_g) / h\theta
\]  

(4)

where \( B \) is a constant and \( E_g \) is the bandgap. In terms of indirect transition, \( n \) equals to 2. By plotting the correlation curve between \((\alpha h\theta)^{1/2}\) and \( h\theta \) and taking the point \((\alpha h\theta)^{1/2} = 0\) by linear fit close to the absorption edge, the values of \( E_g \) can be calculated.\(^{16}\)

6. EXPERIMENTAL SECTION

We investigated 980 nm PC-LD with a stripe width and cavity length of LD of 90 \( \mu \)m and 4 mm, respectively. The RF Plasma-enhanced reactive magnetron sputtering system for the Hengyue vacuum SPT700 model was used to grow the films, the structure diagram of the machine is shown in Figure 1. First, plasma pretreatment has been implemented to eliminate defects and improve the cavity surface quality. After that, SiN\(_x\) films with different \( x \) were coated on the LD facets. Then Ta_2O_5 and SiO_2 films were grown on SiN\(_x\), in succession. The magnetic field intensity of the interface as well as absorption related to the thickness of the film should be reduced as much as possible, so 30 nm SiN\(_x\) was grown. According to the reflectivity formula relating to the maximum light extraction efficiency of LDs,\(^{24}\) the reflectivity of the three-layer films was set to 1%. Finally, post annealing treatment were used to improve the film quality.

In our experiment, the target material (Si target with purity of 99.99%) was bombarded by an electron gun with Ar\(^+\), producing Si atoms. At the same time, N\(_2\) gas was ionized into N\(^+\) by an RF ion source and accelerated by a magnetic field, then the Si atoms combined with N\(^+\) to form SiN\(_x\), and pushed to the substrate by ionized ions. Table 1 lists the process parameters. To a certain extent, the refractive index reveals the structural compactness and stoichiometry of the film, and the extinction coefficient reflects the selective absorption of the electromagnetic wave by matter. Therefore, we mainly focused on the effect of process parameters on the film refractive index and extinction coefficient, both the absorption coefficient and bandgap can be calculated.

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■ ACKNOWLEDGMENTS

This work is supported by the National Key R&D Program of China (2016YFA0301102), National Natural Science Foundation of China (grant nos. 61535013 and 91850206).

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