Study on hydrogen sulfide plasma passivation of 790-nm laser diode cavity surface

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Received August 30, 2007

In order to improve the optical properties of the III-V laser diodes (LDs) by means of H_2S plasma passivation technology, H_2S plasma passivation treatment is performed on the GaAs(110) surface. The optimum passivation conditions obtained are 60-W radio frequency (RF) power and 20-min duration. So the laser cavity surfaces are treated under the optimum passivation conditions. Consequently, compared with unpassivated lasers with only AR/HR-coatings, the catastrophic optical damage (COD) threshold value of the passivated lasers by H_2S plasma treatment is increased by 33%, which is almost the same as that of $(NH_4)_2S_x$ treatment. And the life-test experiment has demonstrated that this passivation method is more stable than $(NH_4)_2S_x$ solution wet-passivated treatment.

OCIS codes: 140.5960, 240.6700, 140.3380.

Usually III-V semiconductor laser cavity surfaces exhibit a high density of states located near mid gap, which often leads to catastrophic optical damage (COD) and affects the lifetime of the lasers[1−4]. The aim of passivation technology for laser diodes (LDs) is to depress the interface state densities within the band gap, prevent their formation, and protect the cavity surfaces of lasers from contaminating with the atmosphere. Some passivation methods have been used to reduce GaAs surface state densities and surface recombination velocity, such as $(NH_4)_2S_x$ solution wet treatment[5,6], hydrogen plasma[7] or hydrogen sulfide plasma treatment[8]. The solution passivation of $(NH_4)_2S_x$ has shown better performance with exhibiting less leakage current in p-n diodes[9,10]. However, some problems have still remained, such as poor reproducibility, fast aging, and surface contamination with heavy metals. As for a dry surface passivation, there is a high degree of reproducibility in control. H_2S plasma dry passivation on GaAs surface was reported and there was a long lasting passivating effect[8]. However, no specific devices were studied except for GaAs surface in Ref. [8]. This paper describes the application for the H_2S plasma passivation technology to the cavity surfaces of LDs.

Theoretically, H_2S plasma atmosphere may consist of H^+, HS^-, and S^{2-}. Possible reactions include: H^+ combines with oxygen in the oxidation layer of the GaAs surface to form H_2O so as to extract oxygen; HS^- or S^{2-} further combines with dangling bonds of Ga or As to form Ga_xS_y or As_xS_y. Compared with immersing treatment in $(NH_4)_2S_x$ solution, it can also form sulfur passivating layer. This passivating process is performed in vacuum, which can avoid other impurities. The process parameters such as time and power can be controlled by computer, therefore, is highly reproducible.

At first, H_2S plasma dry passivating treatment on n^+-GaAs(110) ($n = 1 \times 10^{18}$ cm^{-3}) substrate was investigated. After conventionally etching samples in H_2SO_4:H_2O_2:H_2O = 3:1:1 solution, the sample was placed into the chamber of magnetron sputtering equipment. At 2×10^{-5} Pa of the base pressure, the sample surface was cleaned with argon plasma under 20-W radio-frequency (RF) power, the H_2S gas was then excited by RF power from 0 to 100 W at 0.5 Pa for duration of $1 - 30$ min and an *in-situ* anneal was done at 200 °C for 30 min. The effect of passivation was characterized by photoluminescence (PL) measurements. Surface analysis was performed by Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). At last, the obtained optimum passivation condition was 60-W RF input power and duration of 20 min.

The laser samples used were MBE-grown 790-nm wavelength AlGaAs/GaAs LD chips with a large optical cavity (LOC) broad-waveguide structure. After a conventional process, the wafer was cleaved into bars under the nitrogen atmosphere, which were mounted on self-made clamps, and immediately placed them into the chamber. After the laser cavity surfaces were treated according to the optimum passivation condition, an in-situ annealing was done. Sputtering a monolayer ZnS AR coating and three pairs of a-Si:H/SiO_2 HR coatings were done to optimize the output properties of the prepared devices. Finally, single chip was cleaved for devices characterization.

In order to find optimum passivation condition for H_2S plasma treatment, the PL intensity of (110) oriented n^+-GaAs samples as function of the H_2S plasma exposure time and the plasma RF power under a fixed annealing condition at 200 °C for 30 min in Ar ambient is shown in Fig. 1. The testing temperatures were all 10 K. It can be clearly seen that both the too long exposure time and too high plasma power negate the beneficial effects of H_2S plasma passivation due to the plasma-induced damages. Especially, the high RF plasma power (100 W) severely decreases the PL intensity of GaAs(110). It can be concluded that the high energy ion is the major cause for

1671-7694/2008/030183-03 © 2008 Chinese Optics Letters

the plasma-induced damages. In our case, H_2S plasma treatment at 60-W RF power and 20-min duration is the optimum condition.

Surface analysis by AES and XPS was performed before and after the passivation, the passivation effects of $(NH_4)_2S_x$ and H_2S plasma treatment are shown in Figs. 2 and 3, respectively. AES analysis way can do an element half-quantitative analysis according to Auger electron intensity and atom concentration of the samples. Figure 2 shows the AES spectra from GaAs surfaces prepared by (1) unpassivated sample, (2) passivation treatment by $(NH_4)_2S_x$, (3) passivation treatment by H_2S plasma. As shown in Fig. 2-(1), the unpassivated sample is covered with carbon and oxygen. These carbon and oxygen contaminations, however, are removed sufficiently by surface passivating as shown in Fig. 2-(2) and (3). The intensity of the sulfur signal on the surface is comparable to that of $(NH_4)_2S_x$ treatment. The results show that surface passivating with H_2S plasma is almost as good as $(NH_4)_2S_x$ treatment in terms of carbon and oxygen reductions.

XPS analysis way can find out the element composing content and chemical conformation through measuring the produced photon energy of samples. The chemical

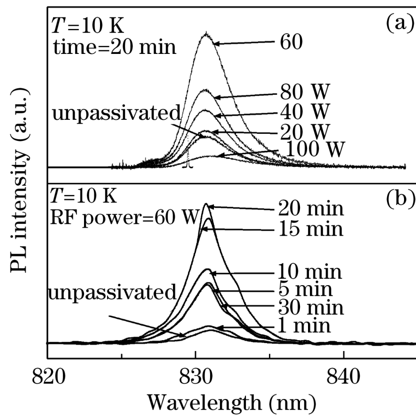

Fig. 1. Measured PL spectra from n^+-GaAs(110) ($n = 1\times10^{18}$ cm^{-3}) (a) under different RF input powers at 20-min plasma exposure time; (b) under different durations of H_2S plasma treatment at 60-W RF input power.

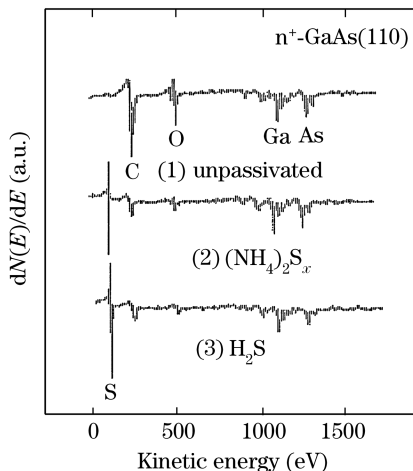

Fig. 2. AES spectra from GaAs(110) surfaces. (1) Unpassivated sample; (2) passivation treatment by $(NH_4)_2S_x$; (3) passivation treatment by H_2S plasma.

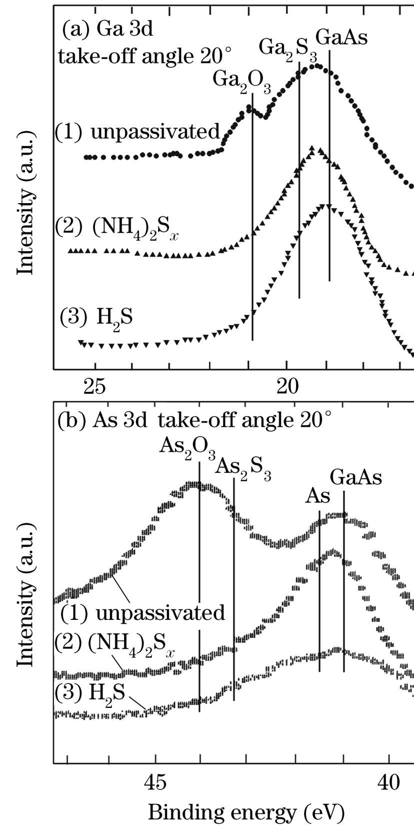

Fig. 3. Angle-resolved XPS spectra of (a) Ga 3d and (b)As 3d core levels from GaAs surfaces. (1) Unpassivated sample; (2) passivation treatment by $(NH_4)_2S_x$; (3) passivation treatment by H_2S plasma.

bonding of the residual sulfur atoms on the surface was investigated by angle-resolved XPS measurements with take-off angles of 20° relative to the average surface plane. The small take-off angle measurements will detect the photoelectron originating from the near surface, indicating the bonds near the surface. Figure 3 indicates that the deposition of sulf-films can be carried out by the H_2S plasma dry-passivated treatment on the GaAs substrate and these sulfur atoms have S-As bonds as the $(NH_4)_2S_x$ treatment as shown in Fig. 3(b)-(2), though we can not identify S-Ga bonds. The XPS studies of $(NH_4)_2S_x$ treated GaAs were reported previously[11−13]. Sandroff *et al.* have investigated that As_xS_y phases can be formed on an oxide-free GaAs surface[11] by the $(NH_4)_2S_x$ treatment, which is in good agreement with our results. Therefore, the H_2S plasma dry-passivated treatment on the GaAs substrate is effective to remove oxidation layer and adsorbed contamination on GaAs surface.

At last, the prepared LDs by different cavity surface treatments are carried on limited test at 100-Hz pulse current. It is found that there is almost the same COD threshold value for both H_2S-treated LDs and $(NH_4)_2S_x$-treated LDs, and compared with unpassivated lasers with only AR/HR-coatings, which is increased by 33%. The results show H_2S plasma passivation technology alike $(NH_4)_2S_x$ solution treatment can depress the interface state densities of the LD cavity surfaces and surface non-radiation recombination velocity and reduce the thermal

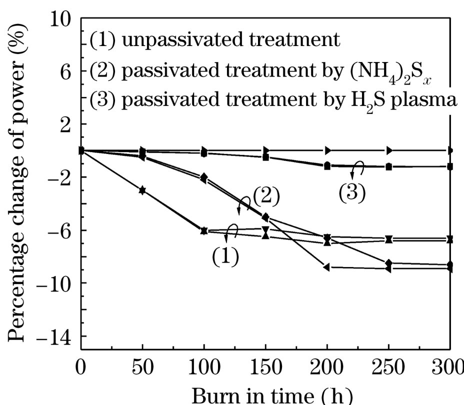

Fig. 4. Aging properties of the prepared LDs by different cavity surface treatments (continuously aging for 300 h at 1.0-A constant current).

creation. So the output power of lasers is improved. To study the effect of different passivation technologies on the stability of the lasers, lifetime experiment was done at 1.0-A constant current for the prepared LDs, as shown in Fig. 4. After continuously aging for 300 hours, it is found that the output power of the devices prepared by $(NH_4)_2S_x$ solution passivation treatment decreases obviously, the percentage change of power is about 10%, and the power drop is more serious than that of unpassivated devices, as shown in Fig. 4-(2). The output power of the devices prepared by H_2S plasma passivation treatment is more stable than others; the percentage change of power is only 1.2% as shown in Fig. 4-(3). The H_2S passivation treatment and subsequent AR/HR coatings deposition are performed in the same process chamber, so the samples are not exposed to air during the whole process. For $(NH_4)_2S_x$ treatment, however, lasers must be immersed in $(NH_4)_2S_x$ aqueous solution, which is difficult to avoid the mixture of other impurities. So a wet-passivated treatment may have disadvantages of poor reproducibility and possible chemical contamination.

In summary, hydrogen sulfide plasma dry passivation applied to GaAs(110) surface and III-V laser cavity facets is effective in removing oxidation layer and improving the optical properties. Compared with unpassivated lasers with only AR/HR-coatings, the COD threshold value of passivated lasers by H_2S plasma is increased by 33%. The results show that surface passivation with H_2S plasma is almost as good as $(NH_4)_2S_x$ treatment in terms of carbon and oxygen reductions. And this treatment has advantages of higher reproducibility and higher stability compared with $(NH_4)_2S_x$ solution wet-passivated treatment.

This work was supported by the National Natural Science Foundation of China under Grant No. 60477010 and 60476026. C. Liu's e-mail address is lclwcw@yahoo.com.cn.

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