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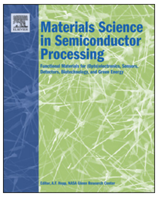

Impurity free vacancy diffusion induced quantum well intermixing based on hafnium dioxide films

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ABSTRACT

Impurity free vacancy diffusion (IFVD) induced quantum well intermixing (QWI) based on electron beam evaporation hafnium dioxide (HfO_2) in the red light diode laser wafer is firstly demonstrated in this work. The red light diode laser wafer had an active region of two 6 nm-thick GaInP quantum wells and three 8 nm-thick AlGaInP quantum barriers. 135 nm thick HfO_2 film was evaporated on the surface of the diode laser wafer at 200 °C. The QWI processes were induced by rapid thermal annealing (RTA) for 20 s at different temperatures. The intensity and the full width at half maximum (FWHM) of the active region emitting wavelength were found increasing and decreasing with the increasing annealing temperature, respectively. When the sample was annealed at 1000 °C, a blue shift of 18 nm was found by the HfO_2 IFVD induced QWI. Moreover, the diffusion lengths and inter-diffusion coefficients were calculated based on concentration distribution in the active region, and the inter-diffusion coefficient values were higher than the results in the Zn impurity diffusion induced QWI.

1. Introduction

Quantum well intermixing (QWI) is an energy band engineering technology to promote different atomic inter-diffusion between the quantum wells and barriers under certain environmental circumstances [1]. As the material constituents can be changed by the intermixing procedure, the QWI technology can be used to adjust bandgap and width of the quantum well region as well as other parameters such as subband energy states, light absorption coefficient, material resistivity, and refractive index. In recent years, QWI technology has attracted increasing attention for the application of various optoelectronic devices, such as non-absorbing windows for high power diode lasers [2], post-growth bandgap-tuned diode lasers [3], monolithically integrated devices and circuits [4], integrated extended cavities for line-narrowed lasers [5], passive C-band quantum well mode-locked diode laser [6], multi-frequency THz emission quantum well chip [7] and multilayer quantum dots optoelectronic applications [8].

Among all methods of creating QWI, impurity free vacancy diffusion (IFVD) QWI has attracted more attention than others as a result of regrowth-free and high crystal quality, and it also has the advantage of simplicity, controllability, and suitability for large-scale production [8]. Although IFVD quantum well intermixing by dielectric caps of SiO_2 or SrF_2 had been reported for the InGaAsP and AlGaAs material [9,10], there is few research on the AlGaInP material based IFVD quantum well intermixing. HfO_2 is a promising material as a high-K gate dielectric, and there exist three phases of cubic phase, metastable tetragonal phase, and monoclinic phase with dielectric constants of 29, 70, and 16, respectively [11]. Whatever the crystal type and phase the HfO_2 film has, its dielectric constant is much higher than that of SiO_2, which has

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potential application prospect in fabricating compatible non-injection windows and non-absorbing windows for high power diode lasers and arrays if the IFVD quantum well intermixing by HfO_2 dielectric cap layer could be implemented successfully.

In this paper, HfO_2 film was firstly introduced in the IFVD quantum well intermixing. The refractive index and transmission of the HfO_2 were acquired by the film deposited on K9 glass, and room-temperature photoluminescence characteristics are investigated and analyzed after rapid thermal annealing (RTA) in different temperatures.

2. Experiments

The laser structure in this work was grown on Si-doped (1 0 0) GaAs substrate with a misorientation of 6° towards (1 1 1)A by low pressure MOVPE. Epitaxial growth was carried out in an AIX200 system which contains a horizontal reactor. During the epitaxy, the growth temperature was controlled at 650–725 °C and the growth pressure was about 10,000 Pa. The source materials were trimethylgallium (TMGa), trimethylindium (TMIn), trimethylaluminium (TMAl), arsine (AsH_3) and phosphine (PH_3). The laser structure contained the following layers: a 100 nm-thick silicon doped n-$Ga_{0.5}In_{0.5}P$ buffer layer was grown lattice matched to the GaAs substrate, followed by a silicon doped 1250 nm n-$(Al_{0.92}Ga_{0.08})_{0.5}In_{0.5}P$ cladding layer; then undoped compressively strained double-quantum-well (DQW) structure [barrier: a 8 nm $(Al_{0.55}Ga_{0.45})_{0.5}In_{0.5}P$ layer, well: a 6 nm $Ga_{0.386}In_{0.614}P$ layer] was sandwiched between two undoped 90 nm-thick $(Al_{0.55}Ga_{0.45})_{0.5}In_{0.5}P$ layers; then a zinc doped 1250 nm p-$(Al_{0.92}Ga_{0.08})_{0.5}In_{0.5}P$ cladding layer and two zinc doped 100 nm p-$Al_{0.2}Ga_{0.8}As$, p-$Al_{0.1}Ga_{0.9}As$ step potential barrier layers, the whole layer structure was terminated by a high zinc doped 120 nm p^+-GaAs cap layer to form Ohmic contact.

In the HfO_2 dielectric cap deposition, compacted and sintered HfO_2 ceramic pellets with a purity of 99.99% were used as the electron beam evaporation source. The laser wafer substrate and the K9 glass substrate were evaporation plated in the same batch for comparison. During the evaporation process, the base vacuum was less than 3×10^{-3} Pa and working pressure under O_2 ambient was about 1.0×10^{-2} Pa. The substrate temperature was automatically controlled at level of 200 °C by applying a heating system. As the initial deposition of HfO_2 was performed at 200 °C without in situ annealing, amorphous HfO_2 film was formed in the two substrates. The thickness of deposited film was monitored by an optical system calibrated by ellipsometer results. The red light diode laser wafer with HfO_2 dielectric cap forms samples for the QWI process, and the sample layer structure is given in Table 1.

The QWI processes were induced by rapid thermal annealing in nitrogen ambient. All the samples were covered with a same GaAs substrate to inhibit the thermal decomposition of laser wafer, and protective atmosphere must be evacuated to detoxify by a neutralization reaction of chemical solution during the annealing processes. The refractive index dispersion characteristic of the HfO_2 film is measured by ellipsometer (J.A. Woollam M2000). The UV–vis optical transmission spectra of the HfO_2 film were recorded by spectrophotometer (Shimadzu UV3150). The room-temperature photoluminescence characteristics of the samples were investigated by fluorescence spectrophotometer (Hitachi F7000). To keep consistent with the measurements of frequency-double Nd:YAG laser exciting photoluminescence, the excitation wavelength was set as 532 nm and the slit was set as 20 nm.

Table 1
Sample layer structure.

Dielectric cap	HfO_2
Cap layer	p+-GaAs
Step potential layers	p-$Al_{0.1}Ga_{0.9}As$
	p-$Al_{0.2}Ga_{0.8}As$
Upper cladding layer	p-$(Al_{0.92}Ga_{0.08})_{0.5}In_{0.5}P$
Upper waveguide layer	i-$(Al_{0.55}Ga_{0.45})_{0.5}In_{0.5}P$
Quantum wells	i-$Ga_{0.386}In_{0.614}P$
Quantum barriers	i-$(Al_{0.55}Ga_{0.45})_{0.5}In_{0.5}P$
Lower waveguide layer	i-$(Al_{0.55}Ga_{0.45})_{0.5}In_{0.5}P$
Lower cladding layer	n-$(Al_{0.92}Ga_{0.08})_{0.5}In_{0.5}P$
Buffer	n-$Ga_{0.5}In_{0.5}P$
Substrate	n-GaAs

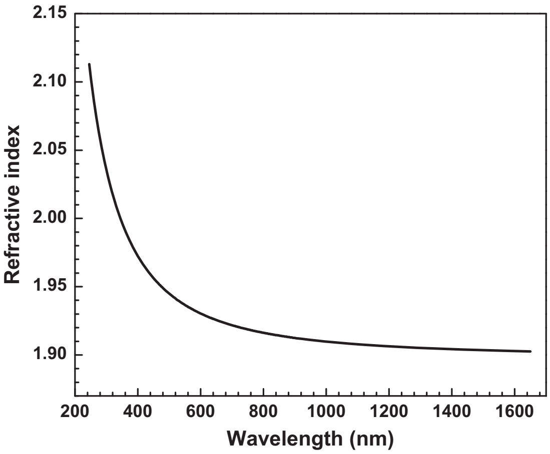

Fig. 1. The refractive index of HfO_2 film as a function of wavelength.

3. Results and discussion

Fig. 1 shows the refractive index of HfO_2 film as a function of wavelength. From 300 nm to 1600 nm waveband where the HfO_2 material does not absorb incident light and the refractive index tends to decrease with the increasing wavelength. For the 632.8 nm which is the emitting wavelength of the He–Ne laser, the measured refractive index is 1.93 and the film thickness is 135 nm. For a more accurate description of the wavelength dependence of the refractive index, the Sellmeier equation can be used, and an empirical formula of

$$n^2(\lambda) = 1 + \frac{1.82586 \times \lambda^2}{(\lambda^2 - 0.01505)} + \frac{0.78876 \times \lambda^2}{(\lambda^2 - 0.01506)} + \frac{33.76992 \times \lambda^2}{(\lambda^2 - 6.93470276 \times 10^3)}$$

is obtained by fitting experimental results.