A new visible photoluminescence in the conducting Ta–Si–N nanocomposite thin films

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ABSTRACT

The conventional visible photoluminescence (PL) behavior at room temperature (RT) is observed in the semiconducting or insulating nanostructured materials with large bandgaps. Here, we have demonstrated the visible-color PL behavior at RT of the conducting Ta–Si–N thin films nanocomposite using simple magnetron sputtering without any post annealing. X-ray diffraction, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Auger electron spectroscopy (AES) depth profile results evidence that the microstructure of conducting Ta–Si–N with a low resistivity of 220–375 $\mu\Omega$ cm exhibits $(Ta_x,Si_y)N$ nanocrystalline grains embedded in an amorphous matrix, which can emit the distinct PL intensity from 390 to 750 nm wavelengths. No PL is detected in the coarse-grain polycrystalline films. Qin's extended quantum confinement/luminescence center model [G.G. Qin, Mater. Res. Bull. 33 (1998) 1857–1866] was adopted and modified to discuss the RT PL mechanism in the conducting Ta–Si–N films using three types of competitive photoexcitation/photoemission processes.

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1. Introduction

The room-temperature (RT) photoluminescence (PL) has been broadly studied these decades for the promising optoelectronic devices in the light emitting or solar cell application [1–6], especially in the silicon (Si)-based material systems suitable for microelectronic integration. The conventional visible PL behavior at RT is observed in semiconducting or insulating materials made of the electrochemical etched porous Si microstrcuture [7–9], post high-temperature annealed chemical vapor deposition (CVD)/ PECVD films with Si nanocrystals (NCs) or quantum dots (QDs) embedded in an amorphous oxide [10–15] or nitride [14–18] matrix. Moreover, since Canham [7] demonstrated that quantum confinement (QC) effect enabled the nanostructured Si emission from bulk's near infrared to visible red light, thousands of papers have been reported on the QC-enabled PL behaviors in Si NCs or QDs from the viewpoints of fabrication [11–18], device [10,16,17] and modeling [11,13]. The combined CVD and post-annealing methods were frequently used to form Si NCs embedded in an amorphous film [11,12,14–18]. The tungsten-doped oxide [11,12] or laser-induced Si NCs formation [19] can be applied to adjust the emission wavelength. Because of the nonconducting PL film with large bandgaps, the coating of conducting transparent oxide or semitransparent metal electrodes [10,16,17] was desired for device integration. Moreover, most of the above semiconducting or

insulating materials were prepared using expensive complicated chemical vapor deposition system as well as post annealing at 700–1000 °C. No conducting material displaying PL at RT is reported so far to the best of our knowledge. In this article, we have successfully demonstrated that the conducting nanostructured Ta–Si–N film is capable of full visible PL, which was used as a conventional diffusion barrier material in Cu interconnection [20,21]. The mechanisms of both conducting electronic transport and PL origins are proposed and discussed for the conducting quasi-amorphous microstructure.

2. Experimental procedures

Boron-doped p-Si (1 0 0) wafers with a thermal oxide layer around 300 nm were used for the reactive cosputtering of Ta–Si–N films in an argon and nitrogen atmosphere at room temperature. Separate Ta (99.99% purity) and Si (99.999% purity) targets were applied by DC power supply and 13.56 MHz RF, respectively. The wafers were biased −150 V during deposition. The nitrogen flow ratio ($FN_2\% = FN_2/(FN_2+FAr) \times 100\%$) was controlled from 2% to 20% in order to study the evolution of microstructure, electric resistivity and photoluminescence of Ta–Si–N films. Three binary Ta–Si, Ta–N and Si–N films were also prepared for comparison with Ta–Si–N. The base pressure and working pressure are 4×10^{-4} and 9×10^{-1} Pa, respectively. The thickness of Ta–Si–N films was 300–400 nm. The microstructure and phase of Ta–Si–N films were identified by grazing incidence X-ray diffractometer (GIXRD, RIGAKU, Japan) using Cu Kα radiation (0.1542 nm). The

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amorphous-like microstructure was also examined by transmission electron microscope (TEM, FEI Tecnai G2 20 S-Twin, USA) using 200 KV LaB_6 Gun. The compositions were analyzed by electron spectroscopy for chemical analysis (ESCA, VG, UK) using Al Kα radiation (1486.6 eV) after surface cleaning by Ar^+ sputtering at 3 KV for about 30 min. The morphology was examined by field emission scanning electron microscopy (FESEM, JEOL, Japan). The element distribution of Ta–Si–N film was examined by the depth profile of auger electron spectroscopy (AES, VG, UK). The electric resistivity was measured by four-point probe method together with Keithley 2400 current–voltage meters. PL spectra was excited by a 50 mW 325 nm He–Cd laser (Kimmon, Japan) at room temperature and measured from 300 to 800 nm through the lens, mirrors, grating and CCD components.

3. Results and discussion

The Ta–Si–N film is a mixture made of binary Ta–Si, Ta–N and Si–N compounds [22]. Fig. 1a shows the GIXRD spectra of the Ta–N, Ta–Si and Si–N films. Only polycrystalline TaN phase in Ta–N was observed with four distinct diffraction peaks while completely amorphous SiN_x was formed with no diffraction peak. Also, only Ta_5Si_3 phase in Ta–Si was found with two broad peaks, which is a characteristic of nanocrystalline grains (nc-grains) embedded in an amorphous matrix (nc/a-matrix), i.e. nanocomposite amorphous microstructure [20]. The identified primary and secondary diffraction peaks' planes of Ta_5Si_3 and TaN in Fig. 1a are labeled in the spectra. The evolution of Ta–Si–N microstructure and phase formation is dependent on the nitrogen flow ratios of $2–20FN_2\%$ (Fig. 1b). Ta–Si–N nanocomposite films with symmetrical broad peaks were formed at $2–6FN_2\%$ while a polycrystalline film was obtained at $20FN_2\%$. The transition of nanocomposite amorphous to polycrystalline microstructure occurred at around $10FN_2\%$ and the asymmetric broad peak appeared.

Fig. 2 shows the TEM image and diffraction pattern of one Ta–Si–N nanocomposite film formed at $3FN_2\%$. The vague rings with tiny spots on the pattern indicate that the microstructure is formed of nanocrystalline grains embedded in an amorphous matrix. Tiny spherical grains of 2–6 nm are dispersed in an amorphous matrix, which lead to the broad GIXRD peaks (Fig. 1b). We have verified [20] that the phase formation of Ta–Si–N at different $FN_2\%$ appears from Ta_5Si_3 phase at $0FN_2\%$, accompanied with Ta_2N at low $FN_2\%$, and then Ta_2Si and TaN at higher $FN_2\%$. The primary nc-grains in the nanocomposite amorphous microstructure are likely Ta_5Si_3, Ta_2N, Ta_2Si or $(Ta_x,Si_y)N$ solid solution for the close peaks. The ESCA-analyzed compositions of Ta–Si–N films at

2, 3, 6, 10 and $20FN_2\%$ were around $Ta_{54}Si_8N_{38}$, $Ta_{53}Si_7N_{40}$, $Ta_{50}Si_5N_{45}$, $Ta_{47}Si_3N_{50}$ and $Ta_{45}Si_2N_{53}$, respectively. The Si/Ta ratio decreases with increasing $FN_2\%$ while the N/Ta ratio increases adversely. Therefore, the large part of amorphous matrix is formed by the disordered Ta–Si–N composite at low $FN_2\%$. Especially SiN_x preferably forms the amorphous matrix [11,23]. The polycrystalline phase in Ta–Si–N at $20FN_2\%$ is made of $(Ta_{1-x},Si_x)N$ solid solution due to low Si content.

The average size of grains in the direction perpendicular to the reflecting planes [24] of the randomly polycrystalline or nanocomposite amorphous phases can be calculated from the Scherrer's Formula ($t = 0.9\lambda/B \cos\theta_b$, where B represents FWHM in radian, θ_b is 2θ of the peak in degrees and λ the wavelength of X-ray in Angstrom or nm) [23–25]. The calculated grain sizes have been widely used for the symmetrical peaks of nanocomposite Me–Si–N [21,23,25] and they exhibit the acceptable values compared to different measurement methods [21,23,26]. The calculated mean grain sizes of $(Ta_x,Si_y)N$ nanocrystals in the Ta–Si–N nanocomposite films at $2–10FN_2\%$ are tiny around
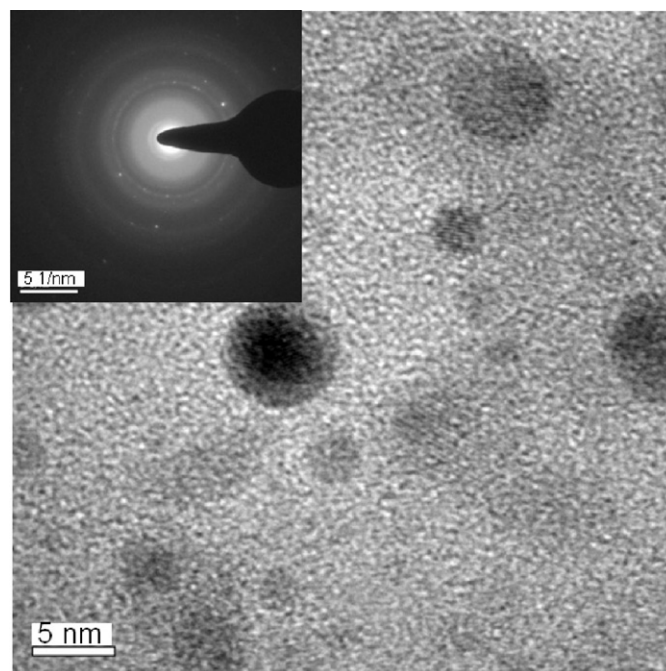

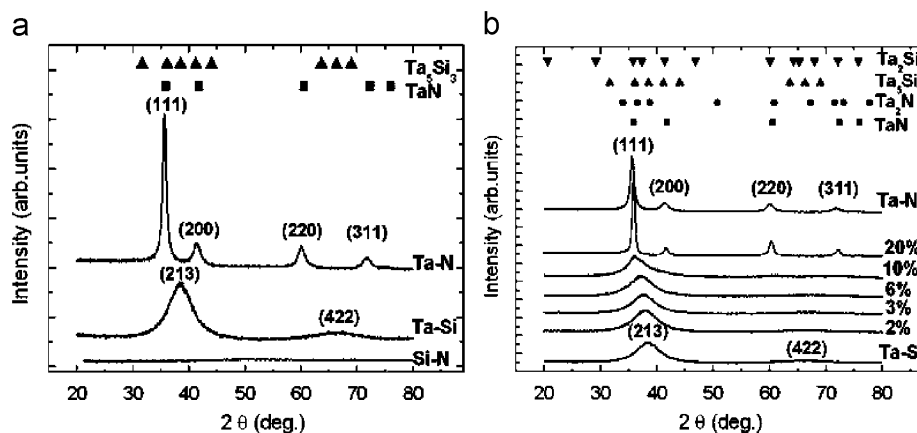**Fig. 2.** TEM image and diffraction pattern of one Ta–Si–N nanocomposite film at $3FN_2\%$.

Fig. 1. GIXRD spectra of: (a) binary Ta–N, Ta–Si and Si–N compounds and (b) five Ta–Si–N films formed at $2–20FN_2\%$ together with Ta–Si and Ta–N films for comparison.