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Study of hydrogen passivation in SiN_x:H films using Fourier transform infrared and photoluminescence spectroscopy

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Amorphous silicon nitride (a-SiN_x:H) films were deposited at 300 °C by plasma-enhanced chemical vapour deposition. Silane/ammonia (SiH_4/NH_3) and silane/nitrogen (SiH_4/N_2) gas compositions were used at various flow rates to study the effect of hydrogen passivation of the films using the photoluminescence (PL) spectroscopy. Fourier transform infrared (FTIR) spectroscopy was employed to derive the relative changes in the total bonded hydrogen (TBH) concentration with increasing flow rates. The composition and the refractive indices of the as-deposited films were also extracted using the bond density calculations from FTIR spectra. The calculated refractive indices of the silicon nitride films were consistent with the ellipsometry measurements. The PL spectra were observed to be free from any interference effect and this was attributed to the nitrogen related defects in all the a-SiN_x:H films. The films deposited using SiH_4/NH_3 showed a higher PL intensity than those deposited in a SiH_4/N_2 environment. A direct relation between the PL intensity and TBH content of the films was found.

Key words: *silicon nitride; PECVD; FTIR; photoluminescence; hydrogen passivation*

1. Introduction

Since the discovery of visible light emission in porous Si [1], intense research activity has been focused on Si nanostructures for their potential application in Si-based light-emitting devices (LED), which is compatible with the current electronic ultra large scale integration technologies [2]. Several prototype devices have been demon-

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strated recently in silicon dioxide (SiO_2) embedded with Si nanostructures, revealing a bright future for Si-based photonics [3, 4]. However, a too large band gap of SiO_2 hinders the injection of carriers, reducing the efficiency and reliability of the devices. In this context, silicon nitride embedded with Si nanoclusters has received great attention due to its smaller band gap and lower tunnelling barrier in comparison with SiO_2 [5]. This makes it more advantageous for carrier injection in electroluminescent devices, often showing intense light emission in the full visible light range in photoluminescence (PL) spectroscopy studies [6, 7]. Thus, Si-rich nitride structures emerge as potential candidates for the development of tunable and highly efficient Si-based LEDs [8, 9]. However, the origin of PL from Si-rich nitride films (hereafter referred as SRN) is still a subject of debate. Though it has been related to the quantum confinement effect of Si nanoclusters in SRN films [10], the radiative lifetime of this SRN structure was found to be much shorter than that of Si nanocrystals [11–13]. Thus there was an apparent ambiguity whether the light emission comes from the defect centres or Si nanoclusters or even from the interface states in the SRN films [14, 15]. Moreover, a thin hydrogenated silicon nitride film on a polished substrate has optical properties similar to those of Fabry–Perot etalon so that it can exhibit interference effect, which may affect the shape of PL spectra substantially [16]. Hence further investigation of the origin of photoluminescence, particularly in light of the interference effect, is of utmost importance.

The present study aims to clarify and classify the origin of PL in amorphous silicon nitride (a-SiN_x:H) films, deposited under identical conditions, using plasma enhanced chemical vapour deposition (PECVD) technique in ammonia (NH_3) and nitrogen (N_2) ambience in the presence of silane (SiH_4). Though there were several reports which showed that there existed a substantial difference in the hydrogen passivation of SiN_x:H films deposited in NH_3 and N_2 atmosphere [10, 17], there have been very few works that related the dependence of PL intensity on the hydrogen passivation of those SRN films [18]. In this paper, we present a comparative study of hydrogen passivation in a-SiN_x:H films deposited using the two gas systems mentioned above. Chemical bonds in the films were examined with the aid of a Fourier transform infrared (FTIR) spectrometry, and room temperature photoluminescence spectroscopy was employed to investigate the dependence of PL intensity on the hydrogen passivation of the SRN films, and from which a direct relation was found between the PL intensity and the hydrogen content of the films.

2. Experimental

The silicon nitride films were prepared using argon-diluted 3% silane with ammonia and argon-diluted 3% silane with nitrogen at the purity in excess of 99.9999%, as the reactant gas sources. Hereafter the SiH_4/NH_3 and SiH_4/N_2 deposited samples will be referred as samples A1, A2 and A3 and samples B1, B2 and B3, respectively. The depositions were carried out on RCA cleaned Si(100) wafers kept at 300 °C. The operating frequency, the RF power and the pressure were maintained at 13.56 MHz, 120 W and 0.3 Torr, respectively. Whereas only the gas flow rate ratios *R*(NH_3/SiH_4) and *R*(N_2/SiH_4) were set to 6.76, 10.14, 13.52 for samples A1, A2 and A3 and set to 27.8, 37, 46.3 for samples B1, B2 and B3, respectively, the flow rate of SiH_4 was kept at a fixed value of 10.8 sccm for both kinds of samples. The thicknesses *t* of the samples A1, A2 and A3 and samples B1, B2 and B3 were around 120 nm and 150 nm, respectively, as measured by a Stylus profilometer. An ellipsometer using 632.8 nm light (Sentech, Laserpro-37-001) was employed to determine the refractive indices of all the samples. Absorption spectra of the samples were obtained using a Shimadzu IR-Prestige-21 FTIR spectrometer at the resolution of 4.0 cm^{-1}. The IR scanning range was from 400 cm^{-1} to 4000 cm^{-1}. PL measurements were performed using a Shimadzu RF-5301PC spectrofluorophotometer under the excitation of the 450 nm line of a 150 W Xe lamp at room temperature. The amorphous nature of the as-deposited silicon nitride films was confirmed from the broad hump-like feature exhibited in X-ray diffraction studies.

3. Results and discussion

3.1. FTIR Analysis

Figure 1a shows the FTIR spectra of nitride films deposited using NH_3 and Fig. 1b shows the corresponding spectra for the films deposited using N_2. The figure exhibits the presence of N–H and Si–H bonds responsible for the hydrogen content present in these films. In samples A1, A2 and A3, the peaks for the stretching modes of Si–H and N–H bonds appear in the range 2330–2357 cm^{-1} and 3330 cm^{-1}, respectively, with a broad Si–N stretching peak centred at 854 cm^{-1}.

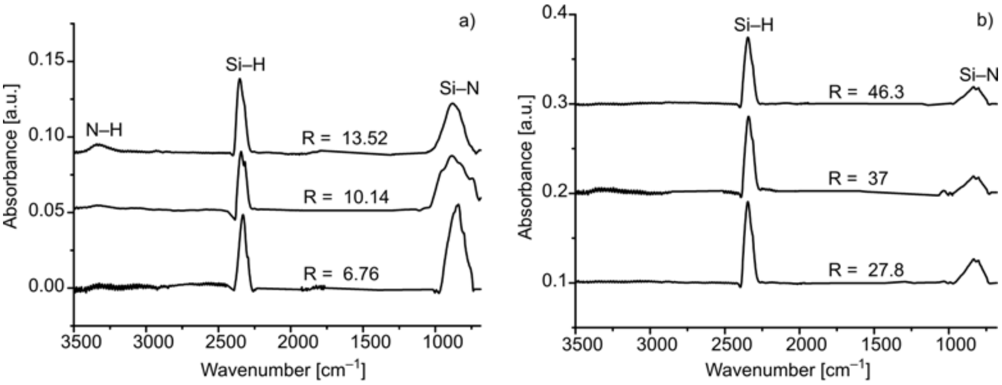

Fig. 1. FTIR absorption spectra for SRN films deposited using: a) NH_3/SiH_4, b) N_2/SiH_4 gas systems exhibiting N–H, Si–H and Si–N stretching bonds. It is to be noted that N–H bonds are absent in b)

The absorbance peaks obtained in the samples B1, B2 and B3 are at 2345 cm^{-1} for the stretching mode of the Si–H bond with a broad Si–N stretching peak around 840 cm^{-1}. The peak positions obtained in the FTIR spectra of our samples are very similar to that reported by several groups in FTIR studies of SRN films [18]. It is also to be noted that there is a relative change in the concentration of Si–H and N–H bonds in the silicon nitride films.

The Si–H and N–H bond concentrations were estimated by the integration of the absorbance peaks centred around 2340 and 3330 cm^{-1}, respectively, using the following equations [19]:

$$[\mathrm{Si{-}H}] = \beta_{\mathrm{Si-H}} I_{2340} \tag{1}$$

$$[\mathrm{N{-}H}] = \beta_{\mathrm{N-H}} I_{3330} \tag{2}$$

where I is the integrated absorption and β represents the absorption cross sections with $\beta_{\mathrm{Si–H}} = 7.4\times10^{-18}$ cm^2 and $\beta_{\mathrm{N–H}} = 5.3\times10^{-18}$ cm^2 [20], thus

$$\frac{\beta_{\mathrm{N-H}}}{\beta_{\mathrm{Si-H}}} = \frac{1}{1.4} \tag{3}$$

The total concentration of bonded hydrogen (TBH) in the silicon nitride film equals:

$$[\mathrm{H_{total}}] = [\mathrm{Si{-}H}] + [\mathrm{N{-}H}] = \mathrm{const}\left[I_{2340} + 1.4 I_{3330}\right] \tag{4}$$

Since, in this study, we are primarily interested in the relative change in TBH content under various gas flow rates, it is permissible to ignore the constant and use the sum of the two integrals (total area under the Si–H and N–H peaks) in the FTIR spectrum as a measure of the concentration of TBH (in arbitrary units) in the film as prescribed by Cai et al. [19].

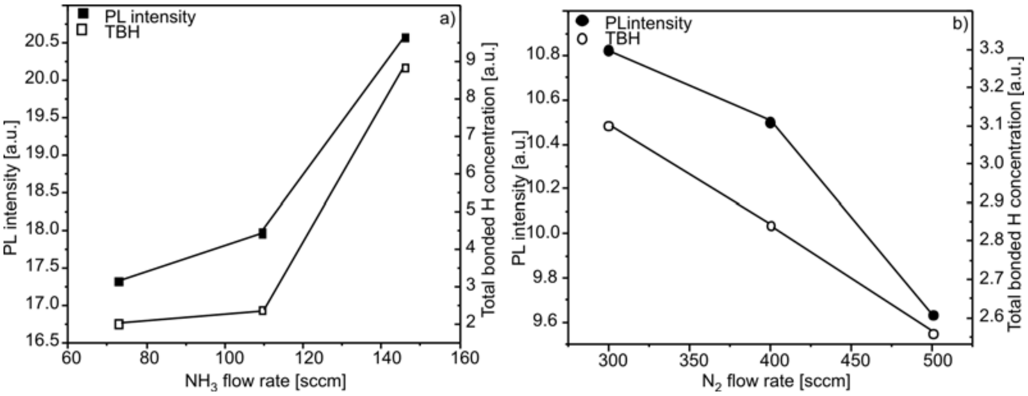

Fig. 2. PL intensity and TBH contents of the SRN films in function of: a) NH_3, b) N_2 flow rates. The figure clearly indicates a direct correspondence between PL intensity and TBH contents of the SRN films

The value of TBH for samples A1, A2 and A3 was found to increase as the gas flow rate ratio $R(NH_3/SiH_4)$ increases, as shown in Fig. 2a. This increase in TBH is attributed to the formation of more N–H bonds as R increases [18]. A close look at the FTIR spectra (Fig. 1) would reveal that samples B1, B2 and B3 contain more Si–H bonds and a negligible amount of N–H bonds. This can be attributed to the choice of improper plasma deposition parameters, namely, RF power and the gas flow rate ratio (N_2/SiH_4) in our study as predicted by Smith et al. [21, 22]. Hence TBH in this case would equal the integral area of Si–H bond only. Unlike the value of TBH for samples A1, A2 and A3, here it was found to decrease as the gas flow rate ratio $R(N_2/SiH_4)$ increased, as depicted in Fig. 2b. This is consistent with a corresponding decrease in Si–H bond area as the gas flow rate ratio R (N_2/SiH_4) increases. Reduction of Si–H bond area can be explained by the displacement of hydrogen atoms from the adsorbing silane radicals as the N_2 flow rate is increased [22].

It is customary to determine the composition x and the refractive index n of the as-deposited SRN films. Though, ellipsometry is generally used to estimate the refractive indices of the silicon nitride films [23], there are several techniques to calculate the composition of the film. Zambom et al. [24] used Rutherford back scattering spectroscopy to extract the composition of their nitride films, whereas Mackel et al. [25] calculated the same composition using the data on the bond densities available from the FTIR spectra of the films through the following equation

$$\frac{[\mathrm{Si}]}{[\mathrm{N}]} = \frac{1}{x} = 0.084\,\frac{[\mathrm{Si-H}]}{[\mathrm{N-H}]} + 0.70 \tag{5}$$

where [Si–H] and [N–H] correspond to the respective bond densities determined from the FTIR spectra. As we have carried out extensive analysis of FTIR spectra of the SRN films, it prompted us to adopt Eq. (5) for estimating the N/Si ratio of those films. Mackel et al. [25] also asserted that there is a relation between x and n such that

$$\frac{[\mathrm{N}]}{[\mathrm{Si}]} = x = \frac{3}{4}\,\frac{3.3-n}{n-0.5} \tag{6}$$

The composition x and the refractive indices for the samples A1, A2 and A3 are estimated using Eqs. (5) and (6), respectively. The variation of the same data as a function of NH_3 flow rate is plotted in Fig. 3. The values of the refractive indices were also obtained from the ellipsometry measurements, which show a variation from 2.20 to 1.98 with the increase in the NH_3 flow rate. It is clear from Fig. 3 that the calculated values of the refractive indices are in close agreement with the ellipsometry-derived values. The increase in the N/Si ratio with the increase in the NH_3 flow rate is attributed to the increase in [N–H] bonds, as is evident from the FTIR spectra (Fig. 1a). Similar correlations between the composition and [N–H] bond densities were also reported by Zhang et al. [23] in silicon nitride films. However, we avoided direct estimation of the composition for samples B1, B2 and B3 using Eq. (5) as it would lead to erroneous result due to the negligible presence of [N–H] bonds in those samples. Instead, Eq. (6) was used to estimate the N/Si ratio from the knowledge of *n*, extracted from the ellipsometry data. Since the refractive indices for samples B1, B2 and B3 vary nominally between 2.0 and 1.95 as obtained from the ellipsometry measurements, the values of *x* turn out to vary only between 0.65 to 0.70, respectively.

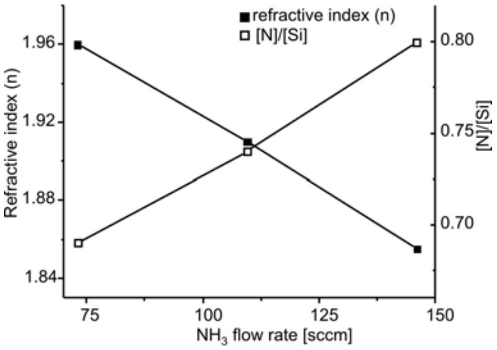

Fig. 3. Refractive index and [N]/[Si] vs. NH_3 flow rate as calculated from Eqs. (5) and (6)

3.2. Analysis of photoluminescence

Figure 4 shows the room temperature PL spectra of samples A1–A3 and B1–B3. A comparison between PL intensities of two typical SRN films, namely, sample A1 and sample B1 is shown in Fig. 5, indicating a stronger visible photoluminescence response for the sample A1 than for the sample B1. A similar trend is also seen for the other sets of samples. The PL intensity in the former case was found to be nearly 1.3 times higher than that in the latter case. This increase is attributed to a better hydrogen passivation in samples A1, A2 and A3, as more N–H bonds contribute to the TBH content [18].

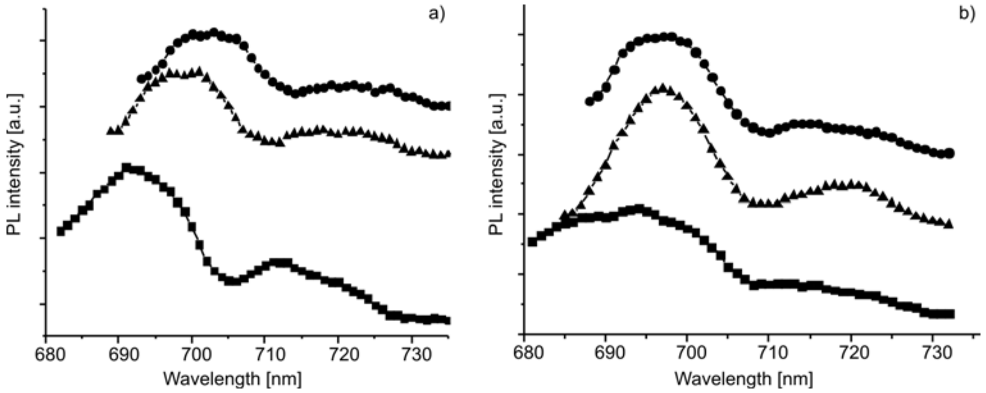

Fig. 4. PL spectra of samples: a) A1 (■), A2 (▲), A3 (●) and b) B1 (●), B2 (▲), B3 (■). The figures show an insignificant shift in the emission wavelengths both in a) and b)

The PL intensity for these samples was also found to increase as the NH_3/SiH_4 ratio increases, as shown in Fig. 2a. This observation is consistent with the increase in the N/Si ratio as the NH_3 flow rate increases (Fig. 3). On the other hand, Fig. 2b shows a small decrease in PL intensity with the increase in the N_2/SiH_4 ratio for the samples B1–B3. This can be explained by a slight decrease in TBH content if there is an increase in the N_2/SiH_4 ratio, where the bonds S–H between the hydrogen and the silicon atoms start breaking as the N_2/SiH_4 ratio increases as mentioned earlier [22]. It is interesting to note that in both kinds of the samples we found a one-to-one correspondence between the TBH concentration and the PL intensity, as clearly exhibited in Fig. 2, though the variations were nominal in samples deposited using N_2. The enhancement of PL in the case of NH_3 deposited samples is clearly due to a greater hydrogen content, as given by the value of TBH, exhibiting a direct dependence of PL intensity on the extent of nonradiative defect passivation of the films, as recently proposed by Kim et al. [18].

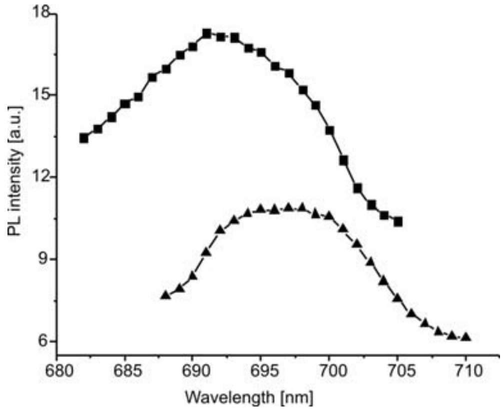

Fig. 5. PL spectra for two typical SRN films, namely, samples A1 (■) and B1 (▲)

It is now important to investigate the luminescence mechanisms in the samples. Generally, luminescence mechanisms have been classified into two types, namely due to radiative defects in the film and due to the quantum confinement effect (QCE) in Si quantum dots [26]. In this context, three main radiative defect energy levels around 1.8, 2.4, and 3.0 eV have been reported for a-SiN$_x$:H films [15]. Pundur et al. [27] also observed two peaks, around 1.75 and 2.0 eV in SRN films using cathodoluminescence, which were also attributed to defect levels.

Before analyzing the emission properties of SRN films to understand the origin of the PL spectra, it is essential to check if there is any interference effect that might have masked the true spectra or have resulted in any additional peak in the PL spectra. Two typical PL spectra corresponding to samples A1 and B2 (Fig. 4a, b) were thoroughly investigated in view of the interference effects by studying how the PL spectra are modified by changing the angle of incidence of light, as prescribed by Marra et al. [28]. The incidence angle with respect to the surface normal was intentionally varied by a small amount from the measurement angle θ and the corresponding PL spectra were recorded. When the original PL spectra (Fig. 4a) are compared with the new ones, as shown in Fig. 6, it is evident that: an additional peak appears around 596 nm, which was previously absent for these samples, and two broad peaks mask the original peaks, which were situated around 696 nm (ca. 1.78 eV) and 718 nm (ca. 1.73 eV). Moreover, the PL intensity of the samples under investigation is much higher than that for the original PL spectra. These observations closely match the PL spectra resulting from the interference effect in a thin amorphous nanocrystalline silicon film as reported by Golubev et al. [16]. It is to be noted that as the true luminescence spectrum in a film–transparent substrate system can always be reconstructed by straightforward division of the PL spectrum by the experimental transmission spectrum, it was suggested that a sample showing comparatively lower PL intensity will not indicate the interference effect, unlike as observed in our SRN films [16]. It is clear from Fig. 6 that there is no shift in the peak positions compared with those obtained in the original PL spectra. This also supports our conclusion that the original PL spectra of SRN samples are free from interference effects [28].

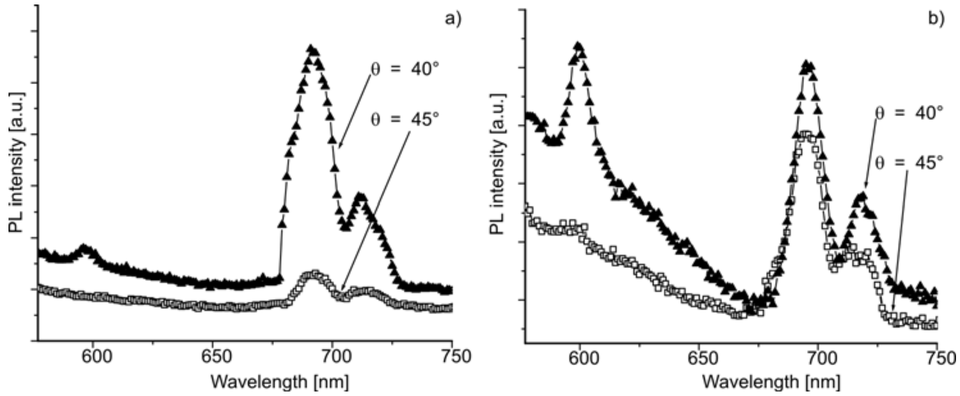

Fig. 6. Combined plot of the original PL spectra (□) and the PL spectra obtained by changing the measurement angle (θ) of light (▲) for the samples: a) A1, b) B2 with thicknesses ca. 120 nm (a) and 150 nm (b)

In the PL spectra of SiN$_x$:H films (Fig. 4) one can observe two peaks, around 697 nm (ca. 1.78 eV) and 718 nm (ca. 1.73 eV) for samples A1–A3 whereas in samples B1–B3, they were found around 696 nm (ca. 1.78 eV) and 718 nm (ca. 1.73 eV). Along with it, an insignificant shift in the emission wavelengths has also been apparent in both kinds of films. This eliminates the possibility that photoluminescence in the as-deposited nitride films was due to any QCE, which is generally associated with a blue shift [18]. The emission peaks obtained near 1.78 eV and 1.73 eV in all samples could be associated with the recombination between nitrogen defect states N_4^+ and N_2^0 which are mostly present in a-SiN$_x$:H films as suggested by several groups [15, 23]. The absence of other defect related peaks, namely around 2.4 eV and 3.0 eV, could be due to the choice of excitation wavelength (450 nm = 2.76 eV) which may not be sufficiently high to excite those defects, as claimed by Wang et al. [29].

4. Conclusion

Silicon nitride films have been fabricated by PECVD using SiH_4/NH_3 and SiH_4/N_2 gas compositions. The composition ratio (N/Si) of the SRN films deposited using NH_3 was found to increase with the NH_3 flow rate, whereas the analogous ratio for N_2 deposited films showed a nominal increase with the N_2 flow rate. The refractive indices of the SRN films vary between 2.20 to 1.98 and 2.0 to 1.95 for samples deposited using NH_3 and N_2, respectively. The PL in both kinds of films is found to be free of any interference effect: this was attributed to the recombination between the nitrogen defect states N_4^+ and N_2^0. The absence of signatures of other defects around 2.4 eV and 3 eV in the films could be related to the inadequacy of the excitation wavelength (450 nm). On changing the gas flow rates, improved PL was observed when using NH_3 as the reactive gas, instead of conventional N_2. This enhancement/suppression of PL intensity in the case of the NH_3/N_2 deposited samples is due to the presence of greater/less hydrogen content, as given by the value of TBH, resulting in a direct correlation between the PL intensity and the TBH content of the films. It is also concluded that the existence of Si–H and N–H bonds could effectively passivate the non-radiative defects in the films. However, to ascertain the role played by the defect states in tuning the PL spectra, it is crucial to investigate how the PL intensity is modified after the samples are annealed at various temperatures. Such investigations are already underway.

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