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Role of ammonia in depositing silicon nanoparticles by remote plasma enhanced chemical vapor deposition

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ABSTRACT

The optimal development of silicon photonics could improve the current state of microelectronics technology. However due to the multiple parameters involved in the elaboration processes, it is not a simple task to fabricate and reproduce silicon emitting structures. In this paper we discuss the role played by ammonia in depositing silicon nanoparticles (Si-NPs) embedded in silicon nitride matrix by remote plasma enhanced chemical vapor deposition (RPECVD). We found that by varying the ammonia flow, the deposition rate changes. It was observed by high resolution transmission electron microscopy (HRTEM) that higher density and a lower average size of Si-NPs is achieved by increasing the ammonia flow. We recognized a linear behavior between the ammonia flow used to deposit a sample and its maximum photoluminescence (PL) emission peak. Finally we propose a model that allows to predict the maximum PL peak for a given ammonia flow within the range of 403–540 nm.

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1. Introduction

The photoluminescence (PL) from silicon nanoparticles (Si-NPs) has kept the interest of the scientific community in implementing these structures as artificial light sources of low cost and in today's microelectronics as optoelectronic devices [1–4]. Previous studies have shown that systems of plasma enhanced chemical vapor deposition (PECVD) and remote PECVD (RPECVD) are very reliable methods for the deposition of Si-NPs embedded in different insulating matrices as nitride silicon (SiN_x) and silicon oxide (SiO_x) [5–7]. The use of these systems to deposit Si-NPs involves several parameters among which are: the flow of source gases, RF source power, deposition chamber pressure, substrate temperature or deposition time. Therefore it is essential to know the role they play, in order to estimate the behavior of the resulting films when one parameter is varied. Some insights about how the deposition parameters are correlated have been implicitly studied by a few authors in their works [8–11] but is still a subject of discussion. In this paper we discuss the role played by ammonia gas flow in the deposition of Si-NPs embedded in chlorinated-silicon nitride thin films (SiN_x:Cl) by RPECVD. We give an explanation of the changes observed in the PL spectra and associate these changes with images of high resolution transmission electron microscopy (HRTEM) to propose a mathematical model to estimate what will be the maximum emission peak in the PL spectrum for a given flow of ammonia gas.

2. Experimental

To conduct this study we deposited five samples on high resistivity (200 Ω cm) monocrystalline silicon wafer n-type (100). The RPECVD system and the method for cleaning substrates have been reported previously [12]. The gas mixture in the plasma consisted of $SiH_2Cl_2/H_2/Ar$ with constant flows for all samples of 5, 20 and 75 sccm respectively. Meanwhile the flow of ammonia (NH_3) was varied from 50 to 500 sccm. The reaction-chamber pressure, substrate temperature and plasma power (RF power) were set at 300 mTorr, 300 °C and 150 W respectively and remained constant for all samples depositions.

A Gaertner L117 ellipsometer equipped with a He–Ne laser (λ=632.8 nm) and an incidence angle of 70° was used to measure thickness and refractive index of the specimens. HRTEM analysis was performed using a JEOL JEM-2010F FasTEM microscope operating at 200 kV near the Scherzer focus with a spherical aberration of 0.5 nm and a theoretical point to point resolution of 0.2 nm that uses GATAN version 3.7.0 as a digital micrograph system for image acquisition. PL spectra were obtained by exciting with a 25 mW power He–Cd laser (λ=325 nm).

3. Results and discussion

Table 1 groups the most important findings of this study. It is possible to identify that the deposition times were different for each of the samples. Variation of deposition time was done

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Table 1
Summary of main results from this study. Ammonia flow for each deposition is specified in the first column. The ratio of the last column is calculated taking into account hundred percent of dissociation of source gases.

Sample	Thickness (nm)	Refractive index	Maximum PL peak (nm)	PL integrated intensity (A.U.)	Deposition time (s)	Ratio NH_3/SiH_2Cl_2
A (50 sccm NH_3)	85.1	1.85	540	$52.05E^6$	720	10
B (100 sccm NH_3)	82.4	1.85	528	$58.04E^6$	510	20
C (200 sccm NH_3)	84.0	1.85	498	$72.21E^6$	330	40
D (300 sccm NH_3)	78.0	1.82	465	$34.23E^6$	240	60
E (500 sccm NH_3)	375.0	1.82	403	$5.63E^6$	900	100

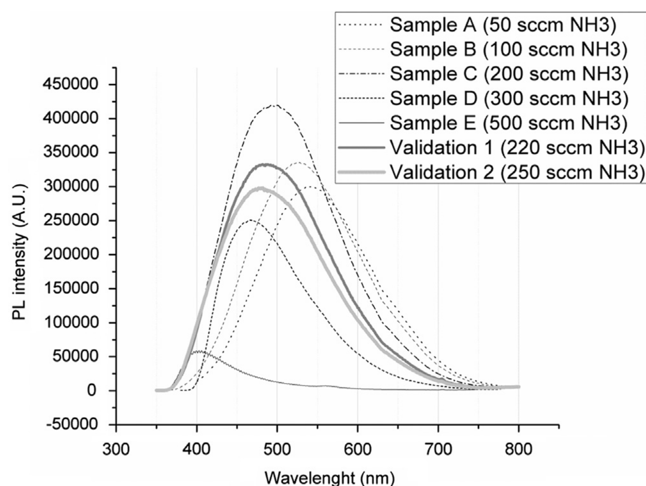

Fig. 1. PL spectra of all samples: specimens A, B, C and D have similar thicknesses ≈ 80 nm. Sample E with a bigger thickness, exhibits multiple peaks caused by interference effects. Validation curves (gray thick lines) exhibit the same behavior than the studied group.

in order to obtain a similar film thickness in all specimens (≈ 80 nm). We chose this thickness for two main reasons. First, to carry out a fair comparison of PL integrated intensity between samples and second to avoid emission interference effects [12]. It is also noted that the sample E has a thickness four times the average, we got it with a longer deposition time.

Fig. 1 shows the PL spectra of all studied samples as well as two specimens from the group used to validate the model we propose later in this paper. Two features are identified at the first glance. First, there is a shift to shorter wavelengths with increasing ammonia gas flow. And second, it is observed that the integrated intensity is different in all samples in spite of their similarity in thickness (except sample E). Previous studies have reported that the integrated intensity is proportional to the density of emitting centers in each sample [13,14], and this may indicate that our specimens have different particle densities.

The above changes are due to variation in the flow of ammonia gas, the only changing parameter of our experiment, and are explained below. In RPECVD systems, the formation of Si-NPs is essentially random. Therefore, it is expected that by maintaining a constant flow of the gas which is providing silicon atoms (SiH_2Cl_2) and increasing the flow of gas which provides nitrogen atoms (NH_3) the probability of achieving Si–Si bonds decreases. By reducing the probability, the average size of self-generated Si-NP is also decreasing. Therefore and according to the quantum confinement effect the PL spectra of samples A, B and C are shifted to shorter wavelengths.

Moreover, the increasing of the PL integrated intensity in the first three samples is because there is a direct proportionality between the decrease of average size and the increase of Si-NPs density. But this proportionality is true only until the N/Si ratio reaches a limit of about 40.

In order to define the exact ratio of the direct proportionality, we carried out a new deposit with 250 sccm of ammonia flow (N/Si = 50). Its PL spectra is shown by the light gray curve in Fig. 1 and the resulting integrated intensity was of $50.92E^6$ A.U. Due to this drop of intensity we deposited another film, with a N/Si ratio of 44 (strong gray line in Fig. 1). Its integrated intensity grew up to $56.94E^6$ A.U. With this last results we are in the possibility to say that the limit of the direct proportionality is 42 ± 2. Beyond this limit nanoparticle density decreases with the increasing of ammonia flow.

The decrease in Si-NPs density is due to the considerable reduction of silicon atoms available in the plasma mixture. However, another important factor is that the plasma power is kept constant and the mass of the gas mixture is increased (by increasing the flow of ammonia) which prevents a total molecule dissociation. An evident effect of this is seen in the plasma brightness, which decreases when ammonia flow rises.

For sample E, the deposition time and thickness were considerably higher than the rest of the samples. The above was because the Si-NPs density reduces drastically when an increment in ammonia gas flow was registered. Therefore the integrated intensity became negligible by keeping the average thickness of the study. Regardless the greater thickness and a lower Si-NPs density, the Si-NPs average size decreases and this reduction is observed in the maximum PL peak that shifts to the shorter wavelength observed in the sample group. To confirm that the shift to shorter wavelengths observed in all samples is effectively due to the decrease in Si-NPs average size, we carried out a HRTEM observation. Fig. 2 shows qualitatively the decrease in the average size of nanoparticles. And therefore the shift could be attributable to the quantum confinement effect.

In the results of Table 1 it is also identifiable that to maintain a constant thickness in samples A–D it is necessary to reduce the deposition time, because the deposition rate changes when ammonia flow changes. This is an expected variation if we consider that more nitrogen atoms are available for binding with silicon. Regardless of the density and the Si-NPs average size, an increase of NH_3 flow is going to promote a faster deposition of silicon nitride thin film.

Moreover, and recalling the impossibility of RF power to dissociate all molecules from source gases when NH_3 flow increases, it is expected that at some point of ammonia flow, the deposition rate reaches an asymptotic limit. This was confirmed by two experiments. First, a deposition with 600 sccm of NH_3; plasma intensity was weak but the deposition was achieved. No PL was registered from this sample, which is an indicative of hundred percent of silicon nitride and a despicable amount of emitting Si-NPs. This film required 180 s to have a similar thickness of the group (81.4 nm) and corroborates the rise of the deposition rate when higher ammonia flow is supplied. The second experiment was an attempt to deposition with 700 sccm of ammonia, the plasma could not be generated with 150 W of RF power. This last

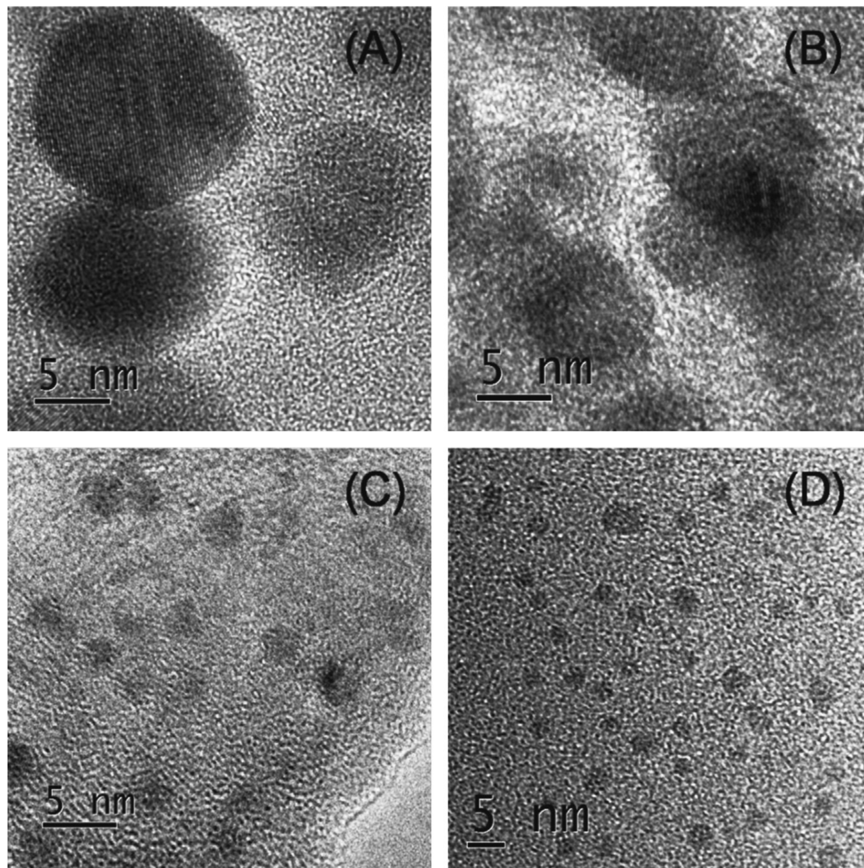

Fig. 2. HRTEM of samples A, B, C and D. Qualitatively it is possible to observe a decrease in the average size of the embedded nanoparticles when ammonia flow rises.

experiment also confirms the incapability of RF power to dissociate all the molecules in gas mixture when its flow rises but the plasma power remains constant.

Control of the emission energy in these structures represents a significant advance for silicon photonics [15,16]. The first effect observed when the flow of ammonia was varied was the shift to shorter wavelengths in the PL spectra. Fig. 3 shows a graph of ammonia flow versus maximum PL peak. Due to the observed behavior we did a linear fit. It was found to have a similarity of 99% with respect to the original behavior. With those results, we present an equation (Eq. (1)) that provides a simple tool to predict what will be the location of the maximum PL peak for any flow of NH_3 in the plasma gas mixture within the range of 403–540 nm. In order to validate the proposed model we deposited seven validation samples with random N/Si ratios between 10 and 100. We estimated the maximum PL peak by using our model (PL Expected) that was compared with the real value (PL Measured). The Mean Absolute Percentage Error calculated from the validation data was of 0.7%. A table with all values of the validation samples is embedded in Fig. 3.

$$\mathrm{MPLp} = -0.3079 \times \mathrm{Aflow} + 557.6328 \qquad (1)$$

It is important to consider that our model is limited not just to the range of wavelengths mentioned before, but to hold all other parameters involved in the deposition process as we did in this work. Furthermore it is of vital importance to remember the considerations we discuss regarding the variations of deposition rate, Si-NPs average size, and particle density when we change the ammonia flow.

Finally, although there is observed a correlation between the Si-NPs average size and the emission energy, it is not possible for us at this moment to integrate this phenomenon in our model. An attempt to integrate the Si-NPs average size has to consider both passivation and crystallinity of Si-NPs that may change with the size variation. Changes in crystallinity modify the effective mass of the charge carriers responsible for the emission, and thus the quantum confinement constant [17].

This result is very promising in the understanding of the role that each parameter plays in the deposition process, which could be all linear. If further investigation could conclude so, the research community would be in the possibility to construct a stronger model involving not just one but two or three parameters in order to accurately estimate the PL peak, thin film thickness and even PL integrated intensity.

4. Conclusion

Some previous studies have superficially addressed the correlations between the deposition parameters involved in the fabrication of luminescent silicon structures. However, the role of ammonia in the deposition of autogenerated Si-NPs embedded in silicon nitride thin films grown by RPECVD had not been discussed as a main purpose of any study. The individual study of each parameter is very important in predicting the properties of the resulting film. This could be useful for lowering costs on experimentation and for adequate reproducibility for possible implementation in devices. In this paper we carried out a discussion about the changes of PL properties occurred in these structures when the ammonia flow is changed. We found that by varying the ammonia flow, the deposition rate changes (high rate achieved when higher flow supplied). The density of Si-NPs increases when ammonia flow increases, up to a certain limit, beyond which the density gradually decreases until films without

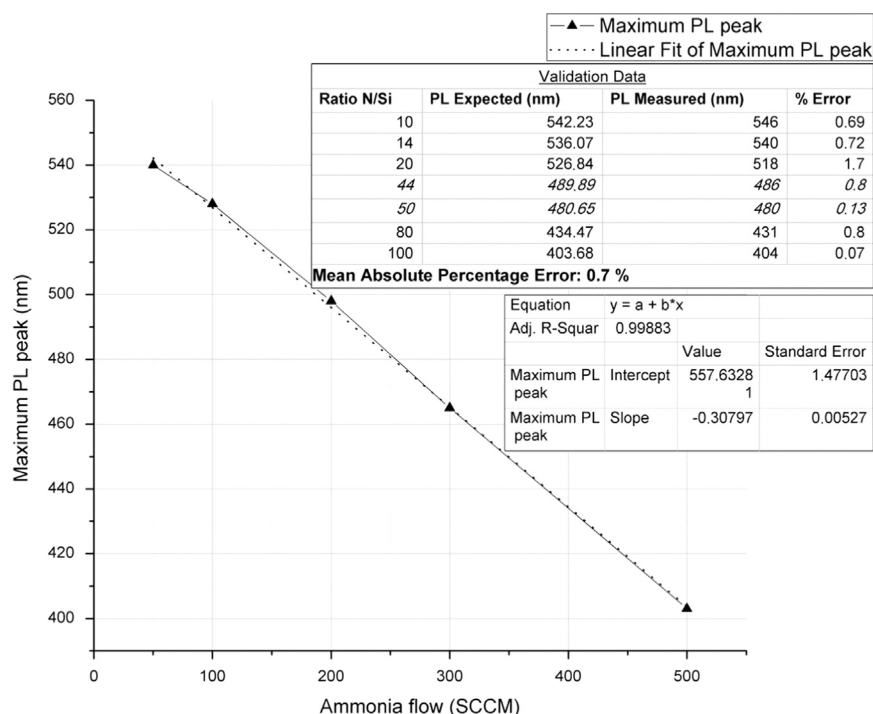

Fig. 3. Ammonia flow used for each sample deposition plotted against the maximum emission peak recorded for the specimen. The dotted line shows the linear fit of the original trend. It also displayed the data used to validate the model and the Mean Absolute Percentage Error of it.

the presence of Si-NPs are obtained. Meanwhile the Si-NPs average size decreases when ammonia flow increases without a boundary. Finally, using our observed data, we proposed an equation which allows to predict the maximum PL peak for a given ammonia flow.

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