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In-Situ Monitoring of Silicon Nanocrystal Deposition with Pulsed SiH_4 Supply by Optical Emission Spectroscopy of Ar Plasma

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Abstract

We performed *in-situ* Ar plasma optical emission monitoring of silicon nanocrystal (SiNC) deposition during pulsed SiH_4 supply. Emission lines from radicals generated by SiH_4 decomposition were observed and enhanced emission of Ar lines which had strong correlation with SiNC formation also appeared. From the correlation the size and deposition rate of SiNCs can be predicted by monitoring the enhanced emission.

1. Introduction

Silicon nanocrystals (SiNCs) have attracted a great interest due to their electronic, optical and quantum characteristics [1, 2]. We have already fabricated SiNCs shown in Fig. 1 by using decomposition of SiH_4 gas in very high frequency (VHF: 144 MHz) plasma [3, 4]. Using pulsed supply of SiH_4 gas, the size dispersion can be narrowed and also the average size is reduced to 5 nm [4].

Plasma optical emission becomes bright when SiH_4 is supplied. We noticed that the duration time is longer than SiH_4 pulse ON time and the intensity become high as the ON time increases. The interactions between SiNCs and plasma have been investigated [5] but not yet when using pulsed SiH_4 supply. Accordingly, we performed *in-situ* measurement of plasma emission during pulsed SiH_4 supply. In this paper, we report the results and discuss the correlations between enhanced emission and formed SiNCs.

2. Experimental

SiNCs were fabricated in VHF plasma cell [3, 4]. The input power was 5 W. Ar gas whose flow rate was 40-90 sccm was supplied continuously to the plasma cell. We used pulsed supply for SiH_4 gas operated by piezo-electric leak valve (Oxford Applied Research, PLV1000) which respond quickly than pneumatic valve. The flow rate of the valve was 6.0 sccm. The pulse ON time was varied up to 50 ms and the interval was fixed to 2 seconds. Fabricated SiNCs were extracted through a 6 mm orifice and deposited on a Si substrate in an ultrahigh-vacuum (UHV) chamber (base pressure: below 10^{-9} Torr; working pressure: around 1 mTorr). SiNCs on the substrate were observed by scanning electron microscopy (SEM) to determine their size and deposition rate.

We also performed *in-situ* measurement of plasma optical emission spectrum by a spectrometer (Otsuka Electronics, MPCD-9800) through a glass window of the cell.

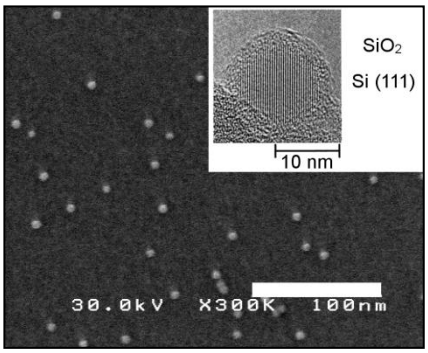

Fig. 1. A SEM image of SiNCs deposited on a Si substrate. The inset shows a TEM image of a single SiNC.

The wavelength range of the spectrometer was 200-810 nm and the detection interval was set to 5 ms.

3. Results and Discussion

Plasma optical emission spectra during pulsed SiH_4 supply are shown in Fig. 2. At 0 ms, spectral lines from neutral Ar (Ar I) are only observed. After SiH_4 is supplied, lines of SiH* (414 nm) and Si* (288 nm) [6] appear (at 45 ms in Fig. 2). Ar lines also start changing, and enhanced emission is observed afterwards. Time evolutions of 414 nm line (SiH*) and 752 nm line (Ar I) are shown in Fig. 3. SiH* emission changes synchronized with SiH_4 supply, but Ar emission enhancement continues longer than SiH_4 ON time. The intensity of this enhancement drastically become strong and its duration time become long as the pulse ON time increases. On the other hand it vanishes when the ON time is short, and then SiNCs are not fabricated although SiH_4 is supplied. Therefore, it is suggested that the enhancement of Ar plasma emission is originated from SiNC formation and there is a threshold density of supplied SiH_4 gas for SiNC nucleation due to the nonlinearity of the nucleation rate to the density of SiH_n (n = 0-2) radicals [7].

We compared properties of the Ar emission enhancement and formed SiNCs in Fig. 4 to investigate the relationship between them. There is correlation between the duration time of enhanced emission and the average size of SiNCs as shown in Fig. 4(a). This result suggests that the emission enhancement appears during SiNC growth. We also notice in Fig. 4(b) that relationship between the intensity of the enhancement and deposition amount of SiNCs per pulse is proportional. From their relationships the size

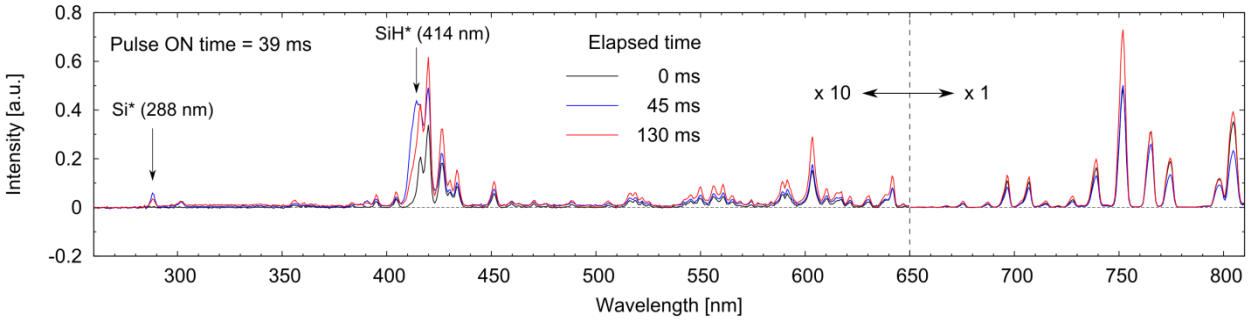

Fig. 2. Optical emission spectra of Ar plasma at 0 ms (pulse start time), 45 ms (peak time of 414 nm line) and 130 ms (peak time of 752 nm line). All spectra except new 414 nm line (SiH*) and 288 nm line (Si*) are attributed to neutral Ar atoms (Ar I).

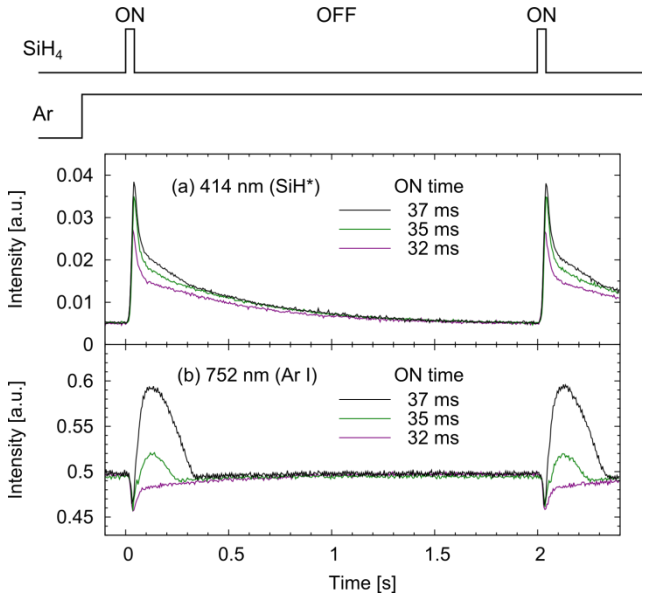

Fig. 3. Time evolution of plasma emission at (a) 414 nm (SiH*) and (b) 752 nm (Ar I). The beginning time of pulsed SiH_4 supply is set as 0 s. Ar flow rate is 90 sccm.

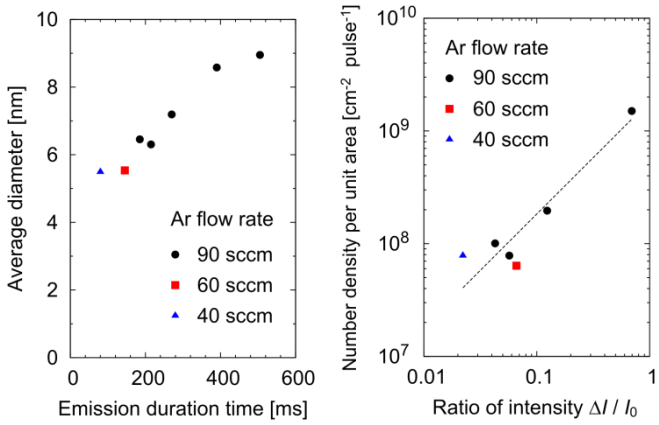

Fig. 4. Relationships between SiNCs and emission enhancement at 752 nm (Ar I). (a) The average diameter versus the duration time. (b) The deposition amount per pulse versus the ratio of intensity. $\Delta I = I_p - I_0$, I_p is peak intensity and I_0 is steady-state intensity. The dashed line is proportional approximation.

and deposition rate of SiNCs can be predicted from the duration time and intensity of the emission enhancement.

The origin of the enhancement can be explained in terms of an energization of the plasma electrons due to the attachment of electrons to SiNCs [8, 9]. When SiNCs are formed by successive insertion reactions of SiH_2 radicals to higher silane molecules, low-energy electrons attach to them and electron temperature increases. As a result, the electron density at the high-energy region increases. Therefore, the number of excited states of Ar atoms also increases and the emission of Ar becomes enhanced.

4. Conclusions

We performed *in-situ* monitoring of SiNC deposition with pulsed SiH_4 supply by optical emission spectroscopy of Ar plasma. Enhancement of Ar emission intensity during SiNC formation was observed. Its duration time and intensity had relations to the size and deposition rate of SiNCs. The enhanced emission is considered to be originated from the SiNC growth. Therefore, it is expected that we can control the size and deposition rate of SiNCs by monitoring the duration time and intensity of the enhancement of the Ar plasma emission.

Acknowledgements

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References

[1] B. Delley and E. F. Steigmeier, Phys. Rev. B **47** (1993) 1397.

[2] L. Pavesi, L. Dal Negro, C. Mazzoleni, G. Franzo and F. Priolo, Nature **408** (2000) 440.

[3] T. Ifuku, M. Otobe, A. Itoh and S. Oda, Jpn. J. Appl. Phys. **36** (1997) 4031.

[4] K. Nishiguchi, X Zhao and S. Oda, J. Appl. Phys. **92** (2002) 2748.

[5] K. Kamataki, Y. Morita, M. Shiratani, K. Koga, G. Uchida and N. Itagaki, J. Instrum. **7** (2012) C04017.

[6] A. Matsuda, Jpn. J. Appl. Phys. **43** (2004) 7909.

[7] M. Otobe, T. Kanai, T. Ifuku, H. Yajima and S. Oda, J. Non-Cryst. Solids **198-200** (1996) 875-878.

[8] B. Layden, V. Cheung and A. A. Samarian, IEEE Trans. Plasma Sci. **39** (2011) 2762.

[9] M. Takai, T. Nishimoto, M. Kondo and A. Matsuda, Thin Solid Films **390** (2001) 83.