Enhancement of Silicon Photon Emission with Nanostructure Array

*Graduate Institute of Electronics Engineering and Department of Electrical Engineering, National Taiwan University, Taipei, Taiwan, 10617, R.O.C.
**Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan, R.O.C.
***Center for Condensed Matter Science, National Taiwan University, Taipei, Taiwan, R.O.C.

ABSTRACT

A Raman scattering enhancement factor up to 4.2 normalized with pure silicon has been achieved by applying the electron beam lithography (EBL) technique to build silicon nanostructure array. Several mechanisms are adopted to explain and discuss the enhancement phenomenon. Through the improvement on the adjustability, uniformity, and stability of the structures, it is expected that a more robust and versatile alternative for the porous silicon materials can be obtained. Although the main purpose of the research is to enhance the light emission efficiency of the silicon materials, an improvement of the Raman measurement sensitivity has also been noticed.

Keywords: Raman scattering, electron beam lithography, nanostructure array, porous silicon

1 INTRODUCTION

Ever since the discovery of its visible photoluminescence at room temperature [1], porous silicon (PS) has been considered a very attractive material for applications in the silicon based optoelectronics. Initiated by this high photon-emission nature of the PS materials and the light transmission enhancement characteristics of the photonic crystals [1] [2], the research of silicon Raman scattering of array nanostructures built by the electron beam lithography (EBL) to improve the emission efficiency has been started. By combining these two special characteristics, the light emission rate limitation of the silicon from indirect band gap transition can be overcome and the equally spaced array structure can act as an optical antenna to enlarge the light emission intensity. In another word, the radiation characteristics of an atom can be changed by modifying the field fluctuations in its vicinity, e.g., by placing it near a surface or a photonic band-gap material [3].

The advantages of EBL built structure are to obtain uniform porosity, hole size and its shape, and those are of variation in PS structures. That random character of the distribution of pores may be the single point to determine the ultimate commercial viability of the porous silicon structures. Another issue should be considered is the aging characteristics of the PS structures. Because PS has an extremely large internal surface area resulting in an instability of its properties with time [4]. Based on previous points of view, a well fabricated tunable structure is expected to be a more robust and versatile alternative for PS structure. The related mechanisms for our photon emission enhancement are also investigated and discussed in our research. Through the improvement in the light emission performance, there is a great potential for the silicon as an opto-electronic component, moreover, because of its compatibility and stability, in principle the silicon nanostructures can be readily integrated with microelectronic circuits.

2 EXPERIMENTAL WORK

For our experiment, a low doped p-type (100) silicon wafer with the resistance value between 1Ω/cm and 10Ω/cm was utilized for the processing, and the sample pattern of 40nm-hole array with 300nm pitch is fabricated by our electron beam lithography system (EBLS), as shown in Fig. 1. Our EBLS is from Elionix, a Japanese company. Various porosity approximation can be easily achieved by our EBLS computer aided designing (CAD) software. The most important point is that the system equips an extremely high capability in building precise array pattern. After the patterning, it was transferred on the substrate by reactive ion etching (RIE) techniques. An SF₆ plasma etching was applied in this recipe. The applied etching time are 90, 150, 156, 168, 180 seconds for six samples respectively. After that, the sample surfaces are cleaned by plasma O₂ treatment. All samples are named according to the etching time, and the SEM pictures of two representative samples are shown in Fig. 2 and 3. Fig. 2 is the picture of “150” sample, in this sample the hole shape tend towards the squares may be attributed to the crystallographic effects [1]. Fig. 3 is the picture of “180” sample. The time of 180 seconds is our longest one, under that condition, the hole structures have become contiguous, meanwhile, the finest rim estimated to be about 20 nanometer size are produced. Actually, it is a tip shaped structure as shown in Fig. 4, and its surface is coated with gold mainly for the observations. This suggests that the structure be of the size smaller than it is estimated.
3 RESULT AND DISCUSSION

Following the nanostructure processing, a Raman measurement including both phonon absorption and emission characterizations has been done. The block diagram of a typical Raman spectroscopy system is shown in Fig. 4. Our measurement instrument, a T64000 type system, is from Jobin Yvon. An argon green light laser with 532 nm wavelength is utilized as the exciting light source. In this research, the light source power is 50 mw. Two of the measured spectra are shown in Fig. 5 and Fig. 6. All six samples are measured in both hole and not hole areas for the sake of comparison. The whole results of our six samples are shown in Fig. 7 and 8. Fig. 7 indicates the raw Raman intensity of the each sample, and Fig 8 indicates the ratio of the Raman intensity by comparing the nanostructure to pure silicon. The result shows that the Raman intensity is approximately proportional to the etching time from 90 seconds to 150 seconds, and a sharp increment starting from 156 seconds was observed. Since it is measured that there is an sharply narrowing down in rim structure, that abrupt change can be reasonably attributed to this cause.

Through the measurement, no Raman shift and asymmetrically broadening of the spectrum were observed. Although it indicates that the obvious quantum confinement effect is not generated in our case, other explanations still can be made in two aspects. The first one is from 90 to 150
seconds, and the enhancement is mainly due to the antenna effect of the array structure, by which the light emission is enlarged in vertical direction, and it is mainly caused by the combination effect of the coupling between the incident light and nanostructures resonance mode (NRM) as well as the coupling between the scattering light and the NRM. The second explanation aspect is from 156 to 180 seconds, and the enhancement is attributed to the combination of both the antenna effect and the rim nanocrystal enhancement effect.

The later effect can be illustrated by applying the Heisenberg principle, which does not allow significant optical transition even for a 2nm microstructure. However, enough mixing of states occurs for various wave numbers in forming quantum confinement, and this makes the optical transition possible \(^{(5)}\). For a nanocrystal size \(d\) related to a momentum \(q = \pm \pi /d\). The position of the Raman peak reflects the area of the phonon dispersion at \(q = \pm \pi /d\). Through the calculation by using same principle, for our nanocrystal size, 20nm, it is estimated that the \(q\) value will be allowed within the flat area as shown in Fig. 9. Because according to the calculation from the relation of

\[\Delta q \Delta x \geq 1/2\]

we can get \(\Delta q\) value about one fortyteth of the whole dispersion range, and the lattice constant of silicon crystal is about 5Å, i.e. the \(a\) value in Fig. 9. It also indicates that the higher density of the state satisfied with the law of momentum conservation, that makes Raman scattering possible, exists within that flat area. For large structure, \(q=0\), therefore, only the zone center phonons are allowed in Raman scattering.

Fig. 5 an anti-stoke Raman Spectrum

Fig. 6 a stoke Raman spectrum

Fig. 7 Raman Intensity profile

Although most of the attentions are paid on improving the light emission properties for the silicon materials’ optoelectronics applications. Another notice should also be taken, that is the application areas on the Raman measurement itself, because the Raman signal usually is very weak, an enhancement on emission efficiency can be for sure to improve the sensitivity of the measurement, and that advantages can be utilized on the surface characterization to control the contamination produced in
the RIE processing, in which a metallic contamination due to the sputtering of the substrate holder at high incident ion energies and a hydrogen contamination which neutralizes the electrical activity of boron near the surface can be generated. \[6\]

4 CONCLUSION

Through the experiment, we have found that the Raman enhancement factor up to 4.2 can be achieved by our currently built structures. The phenomenon can be attributed to two main reasons. The first one is the antenna effect, and the second one is the quantum confinement effect of the nanocrystal. The later effect is acknowledged to be a more dramatic factor to cause this phenomenon. Although the confinement effect is not obvious enough to see the Raman shift and the spectrum broadening, it does have an enhancement factor of 4.2. At the moment, a more detailed analysis work for this research is still carrying on and more experimental works are needed to be done to verify that a well fabricated tunable silicon nanostructure produced by EBLS techniques can be a more robust and versatile alternative for porous silicon materials.

ACKNOWLEDGEMENTS

This work has been supported by the National Science Council, NSC91-2120-M-002-002.

REFERENCES