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This letter reports a new way of preparing wafer sized SiGe quantum dots on an ordered mesoporous sol gel silica coated Si. It was found from x-ray diffraction that very good regular layers of mesoscopic sized SiGe quantum dots can be formed in the silica. Initial low temperature photoluminescence measurements show much improved light emission of the buried dots. This technique is a potential low cost method for producing quantum dot arrays. © *1997 American Institute of Physics.* [S0003-6951(97)02643-0]

Semiconductor quantum dots (QDs) have attracted worldwide attention now due to their suitability for quantum physics study and their potential device applications in both future microelectronics and optoelectronics industry. Si–SiGe QDs,[1] with their technological compatibility to the Si industry, are especially important. Recent research in this field has led to very promising results, such as the efficient Si–SiGe dry etched QD-based light emitting diodes as reported earlier,[2,3] which could potentially be used in all Si-based optical interconnects on Si microchips. It was found that the strong light emission in the dry etched Si–SiGe dots is accompanied by a simultaneous crystalline lattice shrinkage and distortion,[4] which may have effectively created a new lattice structure through the combined effect of strain and dry etching, resulting in an indirect–direct band gap transition. In this letter, we report a low cost QD fabrication technique for creating a similar or new lattice distortion in the SiGe system for light emission application.

We first prepared an ordered mesoporous silica film[5] onto Si substrate by a sol gel process. The film could be spun on or dip-coated on any substrate such as Si, GaAs, normal glass, metal sheet, mica, and many others. In our experiments, the silica film was dip-coated on Si at a wafer pulling speed of about 2 in./min. In the sol preparation, tetraethoxysilane (TEOS), absolute ethanol, H_2O, and HCl were mixed and diluted in ethanol in the presence of a surfactant. The resulted silica material contains regular arrays of uniform porous tubes with the pore sizes controlled by the choice of the surfactant species via intercalation of layered silicates. In this work, we used a mesoporous silica film with pore sizes of $4.5\sim5$ nm. After coating the film onto a Si substrate, we grow a thin SiGe or Ge layer onto the ordered mesoporous silica film at a very slow rate that will allow the SiGe atoms to diffuse into the opening of the mesoscopic porous tubes. In our experiments, we used molecular beam epitaxy (MBE) although the SiGe growth can be done by chemical vapor deposition, and other techniques. The samples were then heat treated to distort the lattice necessary for increasing SiGe based light emission. The post-MBE growth baking helps the formation of a crystalline SiGe or Ge dot array in the porous silica media; any over saturated Ge growth on top of the buried dot array tends to form a larger second dot array, which has also a very high density and dot size uniformity. Initial surface morphology of the sample as examined by atomic force microscope (AFM) shows the presence of a very high density dot array. A typical picture is shown in Fig. 1. Further cross-section scanning electron microscopic examination of the same sample suggests that some of the SiGe dots were formed in the pores. The technological advantages of the QD preparation method are the full Si technology compatibility, low cost, and applications in a range of structures and devices, including magnetic dots for magnetic recording and information storage.

The SiGe dot arrays were then studied by both double axis x-ray diffraction (XRD) and photoluminescence (PL). The XRD was performed on a Crystal Logic powder diffractometer using the 1.125 kW copper $K\text{-}\alpha_1$ x-ray source (which has a wavelength of $\lambda = 0.154\,036$ nm) and a graphite

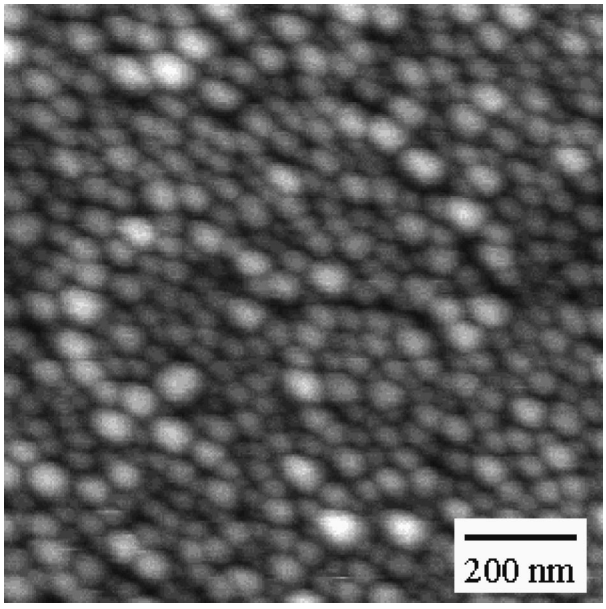

FIG. 1. AFM picture of the top surface of a $Si_{0.5}Ge_{0.5}$ dot sample after heat treatment at 500 °C for 90 min.

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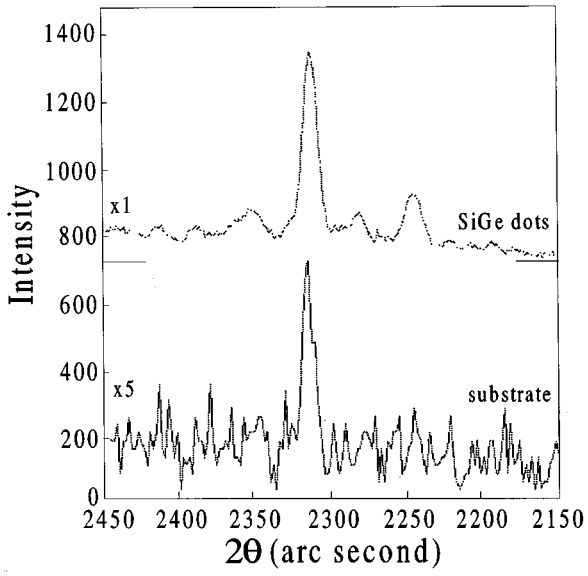

FIG. 2. Comparison of the XRD spectra from a porous silica coated Si substrate and a $Si_{0.5}Ge_{0.5}$ dot sample. The fringes appear around the substrate peak suggests that the dots form regular arrays in the dot sample.

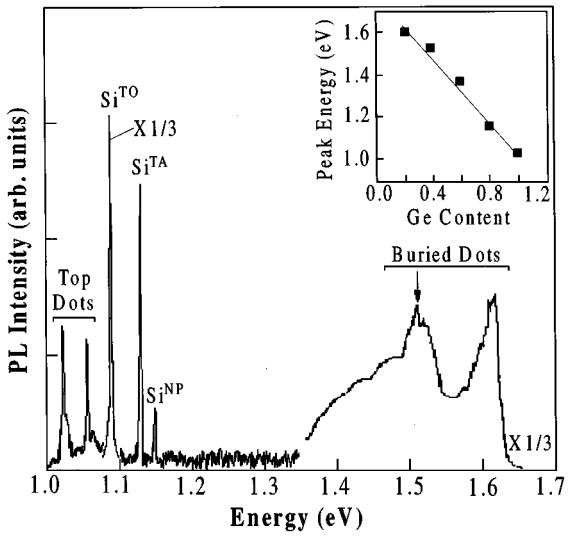

FIG. 3. 4.2 K PL spectrum of a $Si_{0.5}Ge_{0.5}$ dot sample prepared on mesoporous silica coated Si substrate. The sample was post-baked at 500 °C for 45 min.

monochromator. Assuming there are regular layers of SiGe QDs formed in the sample, clear fringes related to the introduction of semiconductor atoms into the sample should be observable.

Shown in Fig. 2 is a comparison of the double axis x-ray diffraction of a $Si_{0.5}Ge_{0.5}$ QD sample and a sol gel silica coated Si substrate in the same region corresponding to the buried layers of QDs in the silica media. It can be found that the $Si_{0.5}Ge_{0.5}$ dot sample has clear observable diffraction satellites up to the second order centered at around 23.65° off the (004) direction of the Si substrate peak, suggesting the formation of very good regular layers of SiGe dots in the sample. We suspect that this diffraction pattern comes from the buried dots inside the mesoporous silica matrix. The inter-dot separation may be decided by the dimension of the inter-connected mesoporous silica tubes which are arranged in such a way that they form layered arrays of pores with the openings of the pores tilted towards the sample surface. SiGe atoms then enter the exposed layered pores to form dots. Other samples with different Ge content in the SiGe alloy are similar to that we described here for the $Si_{0.5}Ge_{0.5}$ dots.

PL has been used to monitor the light emission intensity of these dots. The measurements were done on a standard cryostat system at 4.2 K. The 488 nm line of an Ar^+ laser was used as the excitation with its power density of 4 W/cm^2. The PL signal was detected by using either a liquid nitrogen cooled germanium detector or a GaAs photomultiplier through a 1.5 m monochromator. The slit sizes were kept at 150 μm for all the measurements.

Figure 3 shows a typical PL spectrum of a $Si_{0.5}Ge_{0.5}$ QD sample; there are two set of PL features located in two separated energy ranges. The low energy features resemble the normally observable PL peaks in Si–SiGe heterostructures,[6] which we believe are from the larger over-grown dots in the sample; the higher energy peaks at around 1.5–1.6 eV may be due to the smaller buried dots. The higher energies of the emissions are partly due to quantum confinement and partly due to strain effect introduced deliberately in the dot preparation process. The origins of the higher energy peaks from the buried dots are confirmed by PL measurements carried out on SiGe QD samples with different Ge contents. It was found that the energy positions of the higher energy PL peaks linearly depend on the Ge content in the SiGe, as shown in the insert of Fig. 3.

To optimize the optical emission intensity for possible future optoelectronics device applications, a series of post SiGe growth baking processes has been experimented with. It was found that the PL intensity increases with increasing anneal temperature up to 500 °C (for a fixed baking time), beyond which the PL intensity drops. The optimum annealing time for our samples studied here is about 90 min. This is understandable if one reviews what occurs in the dry etched Si–SiGe QDs. As we know, the mesoporous silica was prepared by a sol gel process and the increase of annealing temperature causes the 'wet' sol gel silica to shrink its pores which are partially filled with SiGe after the SiGe deposition. This drying process of the sol gel silica may alter the SiGe lattice with a compressed strain. Due to the small size of the dots, crystal defects are minimized. From the results of small dry etched Si–SiGe dots, we know that strong light emission can be realized and the strong light emission is always accompanied by a reduced lattice constant and a lattice distortion.[3] The same phenomenon could occur in our current SiGe dots, which may have improved light emission as demonstrated here.

Shown in Fig. 4 is a typical 4.2 K PL spectrum of an optimized Ge dot sample prepared in the ordered mesoporous silica matrix. There are two sizes of dots in this sample, the smaller buried dots in the silica matrix with average pore sizes of about 4 nm and the bigger sized dots over the top of the silica film, which is about 100 nm in diameter on average as seen in AFM. A typical PL of a self-assembled dot sample with similar dot sizes is also shown on the top panel for comparison with that of the bigger dots on top of the silica layer. It is clearly shown that the bigger dots show a broad

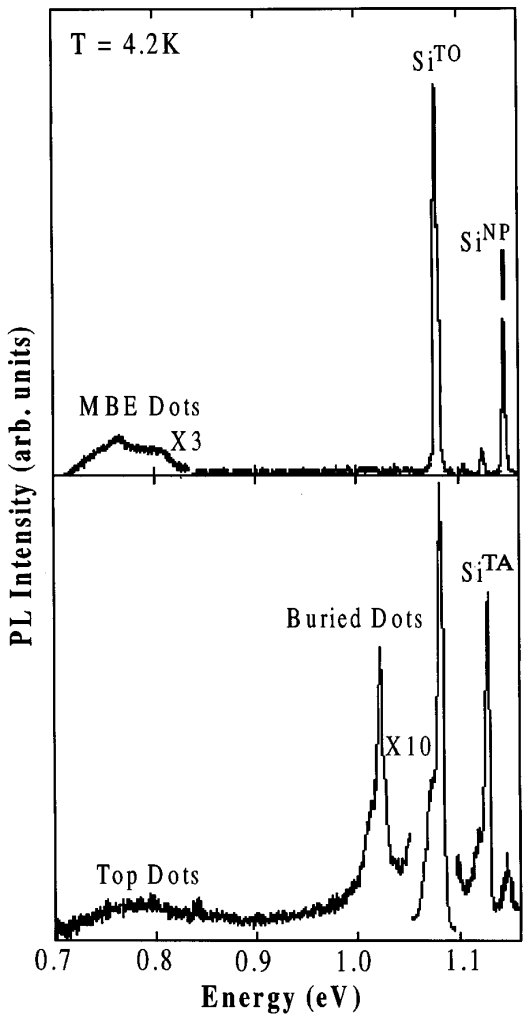

FIG. 4. 4.2 K PL spectrum of a Ge dot sample after baking at 500 °C for 90 min. A PL spectrum from a self-assembled MBE Ge dot sample with similar dot size to the over grown Ge dots is also shown on the top panel for comparison.

band (possibly two unresolved peaks together) emission centered at about 0.78 eV, while an extra peak appears at 1.0223 eV. The latter is about 6.5 times stronger than the broad band. In addition, there is no phonon replica which can be observed on the lower energy side of the strong peak at 1.0223 eV, which is almost exactly what we observed in the dry etched Si–SiGe or Si–Ge dots as reported before.[1] Unlike emissions from an ordinary SiGe system, this is similar to that of a direct band gap material such as GaAs. This indicates that the higher energy peak is from the buried Ge dots in the silica.

The shrinking sol gel silica matrix may have the following possible effects on the buried dots:

(1) altering the band structure of the material system due to strain effect;
(2) the small dot size could also have strong quantum size effects although the inter-dots wave function coupling may also contribute to the improved light emission;
(3) a large distortion in the symmetry of the squeezed dot lattice, making our dots into a totally different crystal structure than Si or Ge and resulting in a direct band gap.

The fact that the phonon replicas, which are usually observable in materials and structures made of the SiGe system, are not present suggest mechanism (3) is involved although there is no direct convincing experimental evidence.

In conclusion, we have proposed a new low cost way of preparing nano-sized QDs suitable for mass production. Our initial experimental result on the SiGe system suggests that SiGe QDs prepared by this method can have much improved light emission which may be the result of the SiGe lattice or lattice symmetry change. The improved light emission from these low cost SiGe dots is ideal for future Si-based optoelectronics devices.

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