Evidence for quantum confinement in the photoluminescence of porous Si and SiGe

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We have used anodization techniques to process porous surface regions in *p*-type Czochralski Si and in *p*-type $Si_{0.85}Ge_{0.15}$ epitaxial layers grown by molecular beam epitaxy. The SiGe layers were unrelaxed before processing. We have observed strong near-infrared and visible light emission from both systems. Analysis of the radiative and nonradiative recombination processes indicate that the emission is consistent with the decay of excitons localized in structures of one or zero dimensions.

A major hurdle in the development of silicon optoelectronic integrated circuits has been the inability to fabricate efficient light emitting devices. This is a direct consequence of the indirect energy gap of this material. Although the problem has been circumvented in other indirect gap materials (notably gallium phosphide) by exploiting the short range central cell potential of isoelectronic impurities in order to produce wave function spreading in **k** space, no such thermally stable impurity system has yet been identified for silicon. Band-gap engineering of confined structures using the Si/SiGe material system may ultimately prove successful, but so far have proved difficult to grow.

Recently, however, reports on the properties of porous silicon surfaces prepared by an electrochemical etching technique, suggest that this process may result in the formation of quantum confined structures which can and do emit strongly in the near-infrared and visible regions.[1] In this letter we report for the first time, that this observation is also true for unrelaxed SiGe epitaxial layers grown by molecular beam epitaxy. We also report optical spectroscopy measurements made to investigate the fundamental nature of the transitions involved. We find that for both Si and SiGe, the data are consistent with localized exciton decay processes. The apparent dimensionality of the confinement is either one or zero dimensions.

Porous silicon was considered some time ago for use as an isolation dielectric in integrated circuits.[2] A thick, insulating oxide film could easily be produced because of the porosity and active nature of the anodized surface. More recently, photoluminescence (PL) in the near-infrared (IR) has been reported[1] and attributed to quantum size effects in free standing silicon quantum wires formed by electrochemical dissolution of bulk silicon. It has also been shown[3] that 110-μm thick layers of this type of structure are translucent to visible light which may indicate an increased band gap compared to the bulk value. The report also explains a self-limiting etching process, where the columns of Si become resistant to further attack when their thickness becomes less than twice the width of the surface space charge region. Under this condition, the quantum wires are depleted of holes and the anodic reaction can no longer proceed.

For the measurements reported here, *p*-type Si of resistivity 2.4 Ω cm and *p*-type $Si_{0.85}Ge_{0.15}$ of resistivity 1.18 Ω cm were studied. Sample preparation was carried out as described elsewhere.[4] In brief, the samples were anodized in 48% HF solution after evaporation of Al on the back surface to ensure a uniform anodic current distribution. The samples were mounted on Teflon plates and coated with wax to prevent current flow from the Al to the HF solution so to perform the anodic reaction selectively on the sample surface. The PL signal was obtained using a 1 m monochromator and a cooled S1 photomultiplier in conjunction with standard lock-in techniques. Excitation was by the 514 nm line of an unfocused argon ion laser with beam powers between 5 and 30 mW.

Each of the anodized samples gave a broad PL spectrum covering a range of energies from near-IR to visible. Figure 1 shows a typical spectrum for each material. It can be seen that the peak in the SiGe PL is at a lower energy than that of the Si but also includes a high energy shoulder. The total charge transferred in the anodization process was 24% greater for the Si/Ge than the Si. We consistently observed that the luminescence was blue shifted with increasing anodization current density, and that for a given sample the peak of the measured spectrum consistently moved to shorter wavelengths as the measurement temperature was increased from 3 to 20 K. The luminescence was also found to quench as the sample temperature was increased, but nevertheless persisted at measurable intensities up to room temperature. A temperature study of the luminescence strength gave a sample dependent activation energy for the quenching of between 34 and 73 meV in the region 150 to 295 K. The data corresponding to 73 meV are shown in Fig. 2. The variation of integrated luminescence intensity with excitation intensity is shown in Fig. 3, and is linear at both low temperature and room temperature. Luminescence decay measurements at low temperature demonstrated nonexponential behavior, with the dominant decay components being between 1 and 10 ns; an

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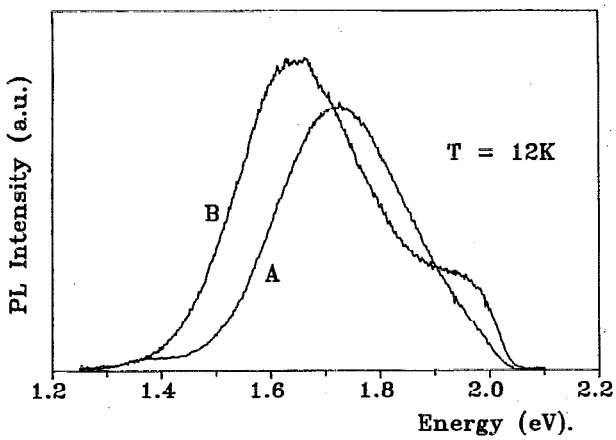

FIG. 1. Photoluminescence spectra taken at 12 K. Curve A is porous *p*-type silicon, and B from porous *p*-type MBE SiGe.

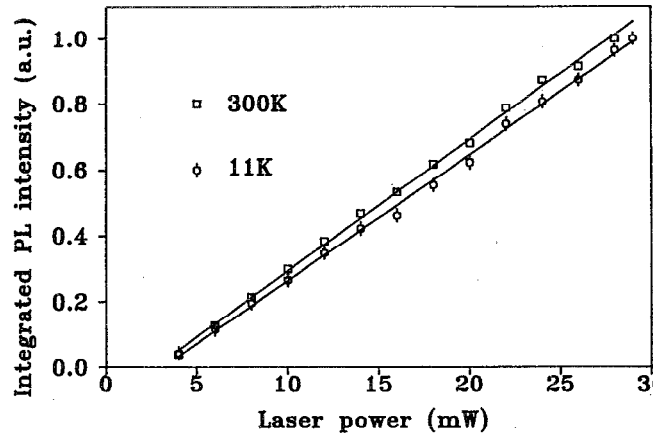

FIG. 3. The variation of luminescence intensity with pump power. The linear relationship also supports the idea that confined excitons may be involved in the radiative process.

example of the decay measured for a silicon sample is given in Fig. 4.

We first attempt to assess our results in terms of highly confined low dimensional excitons. The suggestion that the anodization process produces quantum confined structures is certainly supported by the blue shift in the emitted radiation from samples prepared with a higher anodization current density. If it is assumed that the PL signal originates from quantum size effects in columns of unremoved silicon (quantum wires) then the above observation can be explained as follows. As the current density is increased, the voltage across the interface resistance rises and the area of the pore tip which is forward biased to pass current increases.[5] This results in the formation of larger pores or, in other words, narrower columns of unremoved material, thereby blue shifting the transition energies. If the transition is excitonic, then a linear dependence of PL intensity on excitation density, as shown in Fig. 3, could be expected. The increase in transition energy with temperature is also characteristic of localized excitons thermally populating a density of states associated with microscopic fluctuations in the confining interfaces.[6] In fact this blue shift in the spectrum as the measurement temperature is increased is a commonly observed feature of two dimensional quantum well technology for materials systems in which interface perfection is difficult to attain.[7]

The thermalization data of Fig. 2 are consistent with the delocalization and dissociation of excitons confined in quantum wires. Theoretical estimates of the binding energy of such excitons[8] give a value of 50 or 60 meV for a 50-Å width silicon quantum wire depending on whether the transverse or longitudinal effective mass, respectively, is used in the calculation. These results are in good agreement with our findings. We also note that the thermally activated decrease in the luminescence intensity and the observed short luminescence decays are consistent with exciton dissociation coupled to a strong nonradiative shunt path.

The extremely low density porous layers produced in this work are too fragile to permit direct observation by

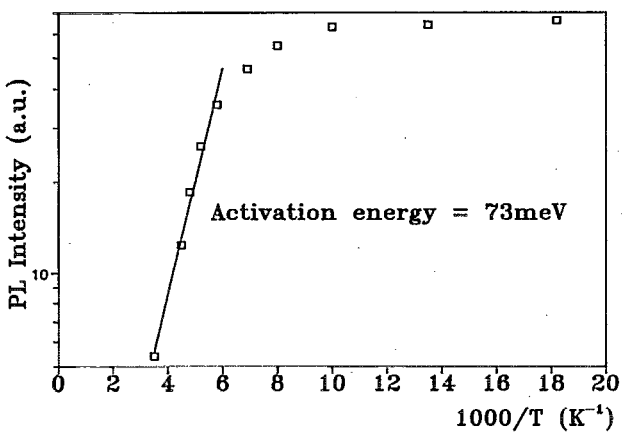

FIG. 2. The figure shows thermalization data for the porous silicon luminescence. The quenching of the integrated PL signal is characteristic of thermal dissociation of the luminescing carrier system, with a competing nonradiative shunt path. The curve suggests that a dissociation energy (in this case 73 meV) can be associated with the quenching process. This energy may be identified with the dissociation of one or zero-dimensional excitons.

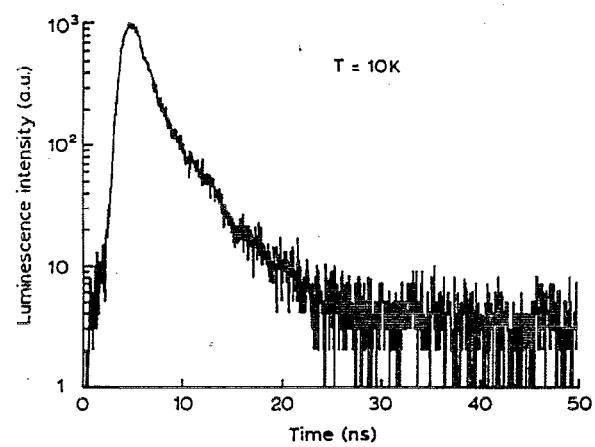

FIG. 4. The luminescence decay of emission from porous silicon. The decay is nonexponential, but is dominated by components of typically several nanoseconds. These data support the view that some nonradiative shunt is present.

standard transmission electron microscopy thinning methods. In view of this we wish to briefly discuss our results in the context of amorphous Si:H, which might be a plausible alternative form for the anodized layers. This material can typically emit a broad luminescence band at around 1.3 eV with a half width of 0.3 eV which also persists at room temperature. However, in contrast to our results, the emission energy has been found to decrease with increasing temperature.[9] This behavior is expected for luminescence associated with band tail states which are generally responsible for optical transitions in amorphous semiconductors. Furthermore, the luminescence decay characteristics contain components which extend from 8 ns to 10 ms. The longer components may be explained by a model which assumes tunneling assisted recombination of spatially separated electron-hole pairs.[9] It must be noted however that the shorter components are comparable with our results. Thermally activated quenching of luminescence has also been observed in *a*-Si:H (Ref. 9) and ascribed to band tails with an activation energy of around 40 meV, comparable to the binding energy which we might ascribe to a low dimensional exciton.

In summary, there are some similarities between our determinations of the optical properties of porous Si and those previously reported for *a*-Si:H. There are also some differences. However, our data are consistent with that expected from the radiative recombination of 1 D or OD excitons confined in free-standing silicon quantum wires. We are therefore able to lend tentative support to this hypothesis. It is clear that a positive conclusion regarding the electronic structure of porous Si must await the results of further investigations.

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