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Fabrication of multiperiod Si/SiO$_2$/Ge layered structure through chemical bond manipulation

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In this letter, we report a method called chemical bond manipulation for fabrication of multiperiod nanometer sized Si/SiO$_2$/Ge layered structure. Chemical bond manipulation is a self-organization process which involves selective breaking and making of surface chemical bonds and thereby enable formation of the desired species on a full wafer scale. We show that oxygen of germanium oxide layer formed on Si(111) are picked up by the Si atoms arriving at the surface during subsequent growth. This phenomenon involves breaking of Ge–O bonds and making of Si–O bonds and leads to the formation of ultrathin Si and Ge layers sandwiched between ultrathin silicon oxide layers, preserving the original wafer morphology. This material exhibits blue-green light emission at room temperature when excited by ultraviolet laser. © 1998 American Institute of Physics.

Light emission from group IV semiconductors has been emerging as one of the important research fields, aimed at developing Si-based optoelectronics technologies. Supraatomic Si has been reported to emit light when it is in nanostructure form and the luminescence behavior is crucially dependent on the nature of the nanometer sized structures. However, controllability of the size of the nanostuctures, interfaces, and surface planarity have posed problems in realizing integrated Si optoelectronic devices. In the area of fabrication of nanostructured materials, control of atomic processes is a key approach to achieving the formation of the desired species. Several researchers have reported nanostructure fabrication by atom manipulation such as using scanning tunneling microscope tip. However, this approach has the main drawback that it is limited to only a very small area of the wafer and involve only a single type of material and therefore is not technologically feasible. Chemical bond manipulation involves a judicious combination of deposition techniques such as molecular beam epitaxy (MBE) and surface phenomena such as chemical reaction. Through manipulation of surface chemical bonds, it is possible to impart functionality to nanostructures by forming different phases of materials such as semiconductor, metal, and insulators which are essential for devices. The growth of Si and Ge was carried out in an MBE chamber. In situ ultraviolet and x-ray photoelectron spectroscopic measurements (UPS and XPS) were performed to characterize the surface species and the reaction pathways. Si(111) wafers (n type, 1–5 Ω cm) were cleaned using standard methods and a buffer layer of ~150 Å was deposited to ensure good quality starting surface. On this sample, 4 monolayers (~6.5 Å) of Ge was deposited at room temperature (RT). The sample was oxidized by exposing to flowing oxygen, outside the ultrahigh vacuum (UHV) chamber, for 1 min. This process resulted in the formation of nearly two monolayers of Ge oxide. The sample was reinserted into the UHV chamber immediately and characterized using photoemission measurements. Si (3 nm) was deposited onto this sample at RT. This procedure (Ge deposition, oxidation, and Si deposition) was repeated seven times (in the case of the sample discussed in this letter, hereafter called as 7-period sample), each time characterizing the surface species. Finally, the sample was capped with Ge (6.5 Å) and Si (5 nm) and ex situ measurements such as cross-sectional transmission electron microscopy (XTEM), Auger depth profiling, atomic force microscopy (AFM), and photoluminescence (PL) measurements were performed. We preferred Si(111) substrate to Si(100) for the growth of multilayers because our previous work showed that bonding partner change reaction performed on Si(100) substrate resulted in considerable surface roughening.

Fig. 1 shows the XPS in the Ge 2p region after oxidizing the Ge covered Si(111) surface [spectrum (a)], and after depositing Si onto the Ge oxide covered surface [spectrum (b)]. Spectrum (a) shows that oxidation results in the formation of a mixture of Ge oxides. On depositing Si onto this surface, Ge–O bonds are broken and Si–O bonds are formed. In other words, oxygen changes the bonding partner from Ge to Si and the signal due to the oxides in Ge 2p spectrum disappears completely. The Ge 2p spectrum returns to that of the same prior to oxidation, implying complete reduction [see spectrum (b) in Fig. 1]. Corresponding Si 2p spectra are plotted in the inset to Fig. 1 and show signal due to silicon oxides after the deposition of Si onto the Ge oxide covered Si(111) surface. The signal due to the oxides in Si 2p is weak compared to that of the Ge oxides because the main peak is dominated by bulk Si. Spectral changes in O 1s as well as UPS corroborate the chemical bond manipulation reaction. This breaking of Ge–O bonds and making of Si–O bonds can be understood based on the large differences in the heats of formation of Ge oxides (for GeO and GeO$_2$, $\Delta H_f = -62$ and $-131$ kcal/mol, respectively) compared to that of Si oxide ($\Delta H_f = -217$ kcal/mol). The strength of the chemical bonds are accordingly different (Ge–O and Si–O, 151 and 191 kcal/mol, respectively). The O 1s core level exhibits a peak around 531.2 eV from oxidized Ge layer and after depositing Si, the peak shifts to 532.4 eV due to the

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formation of Si–O bonds. This was confirmed after comparing with independent oxidation experiments on clear Si and Ge wafers. Changes in the He I UPS further substantiates the occurrence of the reaction. After oxidizing the Ge capped Si(111) and the main signal due to Ge–O bonds is observed at 5.6 eV. Upon depositing Si onto this surface, the main peak is observed at a remarkably different binding energy of 6.6 eV due to the formation of Si–O bonds. Furthermore, cross-sectional TEM pictures as well as AFM images indicate that Si atoms reaching the surface in excess of the reaction with the Ge oxides, form a uniform layer on top of the silicon oxide. By repeating the above procedure, a novel structure consisting of ultrathin Si and Ge layers sandwiched between ultrathin silicon oxide layers, was fabricated (shown schematically in Fig. 2).

Figure 2 is the XTEM image from the 7-period sample, indicating the formation of continuous layers with an interface roughness of the order of atomic dimensions. In Fig. 2 we also show the Auger depth profiling data from this sample. The sharp dips observed in the Si LVV signal due to the depletion of elemental Si and the corresponding peaks in O KLL signal (as indicated by the arrows), show the formation of silicon oxide layers after each deposition of Si atoms. Figure 3 shows the morphology of the clean substrate and the 7-period sample, as observed by AFM [images (a) and (b), respectively]. In spite of the overlayer growth (total thickness ~ 30 nm) and the occurrence of chemical bond manipulation in each period, the final surface of the sample clearly shows the step/terrace structure, similar to that of the starting surface. In other words, the original wafer morphology is preserved throughout the fabrication process. This is mainly because, the chemical bond manipulation is performed at RT, where the atom diffusion rates responsible for interface roughening are considerably reduced. This helps to maintain a smooth interface, reduce the strain in each layer, and thereby maintain surface planarity. This is a
ence is observed at RT with a spectral peak at excitation light from a He-Cd laser. Blue-green luminescence is observed at RT with a spectral peak at 2.7 eV assigned as originating from oxygen vacancy.\(^1\) In our samples, the signal due to Ge oxides\(^1\) is below the detection level in techniques such as electron spin resonance spectroscopic measurements. Tamura et al.\(^2\) reported that hydroxyl groups (−OH) present in the system can cause blue-green luminescence and that is a possibility which cannot be ruled out in our samples.

Figure 4 shows the PL spectrum measured using 325 nm excitation light from a He-Cd laser. Blue-green luminescence is observed at RT with a spectral peak at \(\sim 2.6\) eV (full width at half maximum of the order of 1 eV). The inset to Fig. 4 is a photograph of the light emitting sample at a temperature of 13 K. We recorded the PL intensity as a function of temperature and found that the intensity decreases when the sample is brought to room temperature from 13 K. Additionally, we fabricated samples with different periods (4 and 2) and found that the PL intensity from those samples were significantly low compared to that of the 7-period sample.

We fabricated the multilayer structured samples with varying thicknesses of Si and Ge and performed PL measurements, in order to examine the effect of quantum confinement on the blue-green light emission. We did not observe any shift in the PL peak energy and therefore can rule out the quantum confinement effect as a possible explanation for the light emission. We can also conclude that the emission is not due to nanocrystals/nanoparticles of Si\(^3\) or Ge\(^4\) as the samples do not contain them, as verified by XTEM (the entire fabrication process is carried out at room temperature). We can also exclude the possibility that the emission originates from Ge oxides\(^5\) because XPS results clearly show that Ge is completely in the elemental form (see Ge 2p spectra in Fig. 1). Other possibility for the light emission is defects created at the interface or in the silicon oxide layer.\(^6\)–\(^8\) It is known that defects in SiO\(_2\) matrix and nonstoichiometric oxide of Si (SiO\(_x\) where \(x<2\)) can luminesce efficiently\(^9\),\(^10\) and the emission observed at 2.7 eV is assigned as originating from oxygen vacancy.\(^11\) In our samples, the signal due to oxides in the Si 2p spectrum after the occurrence of the reaction, is a broad feature and therefore indicate the presence of a mixture of suboxides and SiO\(_2\) (indicated by the arrow in the inset to Fig. 1). This may suggest that the emission is suboxide related. Additionally, it is possible that in our samples isolated luminescent species, such as for example, \(E'\) center are created as a result of the bonding partner change reaction. However, such species, if at all present in our samples, are below the detection level in techniques such as electron spin resonance spectroscopic measurements.

![RT PL spectrum from the 7-period sample excited by He-Cd laser (325 nm, \(\sim 2\) mW). Inset shows the photograph of the emission (beam spot size \(\sim 0.5\) mm) taken at a sample temperature of 13 K.](image)