Research Article

Low Temperature (180°C) Growth of Smooth Surface Germanium Epilayers on Silicon Substrates Using Electron Cyclotron Resonance Chemical Vapor Deposition

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This paper describes a new method to grow thin germanium (Ge) epilayers (40 nm) on c-Si substrates at a low growth temperature of 180°C using electron cyclotron resonance chemical vapor deposition (ECR-CVD) process. The full width at half maximum (FWHM) of the Ge (004) in X-ray diffraction pattern and the compressive stain in a Ge epilayer of 683 arcsec and 0.12% can be achieved. Moreover, the Ge/Si interface is observed by transmission electron microscopy to demonstrate the epitaxial growth of Ge on Si and the surface roughness is 0.342 nm. The thin-thickness and smooth surface of Ge epilayer grown on Si in this study is suitable to be a virtual substrate for developing the low cost and high efficiency III-V/Si tandem solar cells in our opinion. Furthermore, the low temperature process can not only decrease costs but can also reduce the restriction of high temperature processes on device manufacturing.

1. Introduction

High conversion efficiency is very important for solar cells, and the multijunction solar cell is a very promising approach from the point of view of high performance. Different energy band gap (E_g) materials can be applied as absorber layers, so that high conversion efficiency can be achieved for multijunction solar cell as a consequence of better utilization of the solar spectrum [1]. III-V multijunction solar cells are the current state-of-the-art photovoltaic devices with a conversion efficiency of over 40% [2]. However, there are still challenging issues that need to be met associated with the low thermal conductivity and high cost of Ge substrates. In order to achieve a low cost and high efficiency solar cell, an attractive choice is the III-V/Si tandem solar cell [3–7], where single junction crystalline silicon (c-Si) solar cells are leaders in the photovoltaic market, comprising at present more than 85% of the photovoltaic market due to the low cost and mature technology of Si processing. Therefore, some researchers have devoted efforts to develop the Ge on Si virtual substrate to solve the lattice mismatched between Si and III-V materials.

Its high carrier mobility and active optical properties have made germanium (Ge) be considered as a promising material for semiconductor devices. There are a number of fledgling technologies being developed that require the epitaxial growth of Ge films on crystalline silicon (c-Si) substrates, such as Ge on Si photodetectors for near infrared (1.3–1.55 μm) sensing [8–10], Ge lasers [11], and monolithic integration of III-V compound semiconductor devices on c-Si
[12–15]. However, the difficulty of growing epitaxial Ge on a Si substrate lies in the 4.2% lattice mismatch between Ge and Si. This may cause two serious issues: high surface roughness resulting from the Stransky-Krostanov growth which would be an obstacle in the application of the Ge material on Si devices and a high threading dislocation density (TDD) in the Ge epilayer that could form recombination centers [1].

Although high quality Ge epilayers have been successfully grown on Si have using molecular beam epitaxy (MBE) [16, 17], ultrahigh vacuum chemical vapor deposition (UHV-CVD) [18–20], and reduced pressure chemical vapor deposition (RPCVD) [21, 22], there are still many challenges that must be overcome. For example, the high growth temperature (usually >550°C) which is not really compatible with standard complementary metal-oxide-semiconductor (CMOS) [20]. To overcome this difficulty, Colace et al. developed an inexpensive low temperature process using the thermal evaporation method to grow Ge films at a lower growth temperature. They successfully obtained an epitaxial Ge structure on a Si substrate at a temperature of about 300–400°C [23, 24], which has been used for near infrared photodetection [24]. However, this technique is not very economical as most of the material is not deposited on the sample. In this work, we use the electron cyclotron resonance chemical vapor deposition (ECR-CVD) to grow the Ge epilayers on c-Si substrates at a low growth temperature of 180°C. The plasma generated in the ECR process is via resonant absorption of a microwave power by electrons in a magnetic field and gas ionization via subsequent electron-atom collisions. By the application of this plasma-generating process, the total working pressure may typically lie in the mTorr range, which is 1–2 orders of magnitude lower than that in the usual parallel-plate plasma-enhanced chemical vapor deposition (PECVD). Because the average mean free path of particles in the gas-plasma phase exceeds the thickness of the plasma sheath, the generated ions are not affected by collisions on their way to the substrate, and they impinge with a rather sharp and well-defined energy distribution. Thus, ECR-CVD enables an improved control of the deposition process. Furthermore, the uniformity of ECR plasma is ±0.3% over 160 mm and ±12.5% over 200 mm as reported by Kawai et al. [25]. These indicate that ECR-CVD can be another choice for the epitaxial growth of Si and Ge films. In our previous studies, we obtained the amorphous to microcrystalline silicon phase transition at a lower hydrogen dilution ratio (H₂/SiH₄ = 0.71) compared with PECVD, demonstrating the high dissociation of ECR-CVD [26]. Moreover, we can deposit the Ge thin films with high crystallinity and conductivity on glass substrates using ECR-CVD [27]. Recently, Platen et al. successfully grew epitaxial Si thin films at low temperature using ECR-CVD [28]. This suggests the possibility of growing Ge epilayers on Si using ECR-CVD.

In this work, we attempt to grow the Ge epilayer on Si at a low growth temperature. Such a Ge epilayer can be used as a buffer layer to solve the lattice mismatched between III-V materials and Si in order to combine these two materials to develop the low cost and high efficiency III-V/Si tandem solar cell which has been reported [29]. Because the bandgap of Ge is 0.66 eV, Ge epilayer thickness for the III-V/Si tandem solar cell should be thin enough to reduce the optical loss. It is difficult to obtain a Ge epilayer with high crystal quality and thin thickness. Therefore, in this study, we used the ECR-CVD to grow the thin Ge epilayer (40 nm) on Si and modulate the working pressure to improve the crystal quality at a low growth temperature which can cost down and overcome some problems with the high temperature process that limit its application in devices.

2. Experimental Details

In this study, we discuss the growth of 40 nm Ge epilayers at a low growth temperature of 180°C using ECR-CVD. A schematic diagram of our system is shown in Figure 1. The vacuum chamber consists of a plasma chamber (cylindrical waveguide is 20 cm in height and 20 cm in diameter) and reaction chamber (cylindrical waveguide is 35 cm in height and 60 cm in diameter). The plasma chamber consists of an overmoded cylindrical microwave cavity, open at one end. Microwaves of 2.45 GHz are introduced into the chamber through a cylindrical wave guide operating in TE₁₁ mode. The chamber is encircled by a main magnetic coil which produces a static, divergent axial magnetic field. A magnetic field of 875 G is utilized to produce ECR conditions.
confining the plasma (keeping it off of both side walls and the microwave window) and forcing the plasma out into the reaction chamber. The two concentric submagnetic coils situated behind the wafer plane are used to control the profile of the magnetic field in the downstream region. One coil is operated in opposition to the main coil, to form a “cusp” field configuration, while the other is operated in concert with the main coil to form a “mirror” field configuration. Both coils can be operated simultaneously to provide complete control over the magnetic field geometry near the wafer. The position of the wafer holder assembly is kept at 22.5 cm from the plasma chamber aperture. The chamber walls are water cooled during the deposition process. Evacuation of the chamber down to the high vacuum regime is performed by a turbomolecular pump providing a residual gas pressure of nearly $2 \times 10^{-6}$ Torr.

Ge epilayers were deposited on a p-type Czochralski (Cz) c-Si (100) wafer (1–10 $\Omega$ cm), and before deposition, the native oxide was removed in a 5% hydrofluoric acid solution. We modulated working pressure via a throttle valve from 15 to 30 mTorr in an attempt to improve the reaction gas dissociation to obtain epitaxial Ge on Si, and the other deposition parameters were as follows: the source gas supplied via an inlet valve upon the ECR region including Ar, H$_2$, and 10% GeH$_4$ diluted with He; the flow rate ratio of H$_2$/GeH$_4$ was 100; the microwave power was 700 W. During the deposition, the plasma distribution was observed using optical emission spectroscopy (OES) and we used $H_{\beta^*}/H_{\alpha^*}$ ratio to represent the $T_e$ to realize the growth mechanism of Ge epilayers. The crystal quality and strain in the Ge epilayer were identified by high resolution X-ray diffraction measurement, Raman spectroscopy, and spectroscopy ellipsometry (SE). XRD measurement is using the incident Cu $K_{\alpha}$ line as the X-ray source (wavelength is 0.154 nm) at 40 kV and 40 mA to obtain the intensity and the FWHM of the Ge (004) peaks and the Ge (004) peak position was used to calculate the strain in the Ge epilayer. The Raman spectra were excited by 488 nm laser line and the power of the laser was kept below 0.5 mW to eliminate the possibility of laser induced crystallization. The surface morphology of Ge on Si was measured by atomic force microscopy (AFM). And the transmission electron microscopy (TEM) was used to observe the Ge/Si interface to demonstrate the epitaxial growth of Ge on Si. For the electrical properties, we study the carrier concentration and mobility of Ge epilayers on Si identified by Hall measurement.

3. Results and Discussion

During the film-growing process, OES was used to monitor the plasma distribution in order to investigate the growth mechanism of the films. The OES intensities of Ge$^*$ and GeH$^*$ are the dissociative excitations of GeH$_4$ molecules. The species of Ge$^*$ and GeH$^*$ are produced by electron impact with GeH$_4$ molecules and the electron energy for formation of Ge$^*$ is more than GeH$^*$. Therefore the Ge$^*/$GeH$^*$ ratio shown in Figure 2 gives an information of reaction gas dissociation. When the growth condition is at the higher working pressure, the mean free path of precursors and electrons is shorter indicating that the collision in plasma is drastic which can dissociate the reaction gas completely. The high dissociation during growth is a benefit to grow an order film, so the film grown with a higher Ge$^*/$GeH$^*$ ratio will result in a better crystal quality and the structural properties of the films will be discussed later.

For the structural properties of Ge on Si grown by ECR-CVD, we used SE, XRD, and Raman spectroscopy to characterize the thickness and epitaxial quality of Ge. SE which is a nondestructive optical measurement technique can identify the crystal quality, thickness, and dielectric constant Ge on Si. Figure 3 shows the Ge epilayer growth rate as a function of working pressure. The growth rate decreases from 0.215 to 0.11 nm/sec as the working pressure increases from 15 to 30 mTorr. Figure 4 shows the imaginary part of the pseudo-dielectric functions of Ge the films compared with crystal
Figure 4: The imaginary part of the pseudodielectric function of Ge epilayers deposited on c-Si (100) substrates for various working pressures as measured by spectroscopy ellipsometry. The spectrum of bulk c-Ge (100) is also displayed as a reference to compare the crystal quality with Ge epilayers.

Figure 5: High resolution XRD rocking curve of the Ge (004) peak with various working pressures. The dash line is the position of unstrained Ge (004) position calculated by Bragg's law. The inset shows the peak intensity and full width at half maximum of the Ge (004) peak from XRD patterns.

Ge measured by SE and fitted by the Tauc Lorentz model [30] and Bruggeman effective medium approximation (BEMA) [31]. The increase of working pressure can improve the quality of Ge epilayer, as evidenced by the increase of the intensity of the two peaks at 2.3 and 4.3 eV characteristic of crystalline Ge. In the pseudodielectric function of Ge, the 1.5 eV to 3 eV part of the photon energy is more sensitive to the thickness of the films, and the 3.5 eV to 4.5 eV part is the information of the epitaxial growth of the Ge on Si films. The higher this peak is, the more the film behaves like a bulk material [32]. By observing Figure 4, we can see an increase of the 3.5–4.5 eV peak when the working pressure is increased, which indicates a better quality of an epitaxial Ge film.

In order to further characterize the epitaxial quality of Ge, Figure 5 shows the XRD $\Omega$–$2\theta$ spectra of the Ge epilayers on Si grown at various working pressures and we fitted the intensity and the FWHM of the Ge (004) peaks. We found that with the increase of working pressure, the FWHM decreases from 1473 arcsec to 683 arcsec, while the peak intensity increases from 57 to 706 arb. unit. This result suggests that the Ge (004) crystal, which is the crystal phase of the epilayer grown on Si, has a better quality at a higher working pressure, and it is consistent with the imaginary part of the pseudodielectric function of the Ge on Si films measured and fitted by SE.

In addition to the XRD measurement, we also used Raman spectra to determine the crystal quality of Ge epilayers. In Raman spectra of Ge, a peak at ~300 cm$^{-1}$ indicates the characteristic TO phonon mode in the crystalline phase of Ge ideally. On the other hand, a broad peak centered around 280 cm$^{-1}$ indicates the amorphous phase of Ge. Figure 6 shows the Raman spectra of Ge epilayer grown with various working pressure and a c-Ge (100) wafer. We used a Lorentzian fit to obtain the FWHM for the Ge TO mode as shown in the inset of Figure 6. By increasing the working pressure, the FWHM of Ge epilayer decreased from 9.95 to 7.95 cm$^{-1}$ and the FWHM of a c-Ge wafer is 6.11 cm$^{-1}$, indicating that the crystal quality becomes better with the increase of working pressure.
In the case of growing epitaxial Si films, the incidence of \( \text{H}_2 \) in the source gas can etch the film-growing surface and help to form stronger Si-Si bonds. Atomic H breaks the Si-Si bonds, causing Si atoms weakly bonded to other Si to be removed. After this, the film-growing precursor, SiH\(_3\), replaces this at the sites to form strong and rigid Si-Si bonds, which leads to a more ordered structure [33]. Because of the similarity of structural properties between Si and Ge, we presume that the growth mechanism of Ge is similar to that of Si. A longer mean free path can lead to a more complete hydrogen etching effect which would probably damage the film-growing surface because of the high hydrogen dilution ratio of \( \text{H}_2/\text{GeH}_4 = 100 \). Therefore, the crystal quality can be improved by increasing the working pressure. The increase of working pressure can decrease the mean free path of the film-growing surface due to the high hydrogen dilution ratio and can dissociate the \( \text{GeH}_4 \) effectively demonstrated by the \( \text{Ge}^*/\text{GeH}^+ \) ratio. With the above results, we can conclude that at a higher working pressure, with a shorter mean free path and effective reaction gas dissociation, better 40 nm Ge epilayer on Si film can be obtained, under a working pressure of 30 mTorr. Compared with other growing methods, for example, UHV-CVD [34], MBE [16, 17], RPCVD [21, 22], LEPECVD [35], or thermal evaporation [23, 24], using ECR-CVD, we can obtain an epitaxial Ge phase in the XRD rocking curve at a low temperature (180°C) simply by increasing the working pressure.

Moreover, we used the XRD and Raman spectra to further analyze the strain in the Ge epilayers. The out-of-plane lattice constant (\( a_\perp \)) of Ge epilayer from Ge (004) can be calculated by Bragg’s law in XRD pattern [22]:

\[
a_\perp = \frac{2 \lambda}{\sin(\Omega_{Ge})},
\]

where \( \lambda = 0.15406 \) nm for Cu \( K_\alpha \), wavelength and \( \Omega_{Ge} \) is the Ge (004) peak position. When the Ge epilayer is relaxed, the peak distance is 5649 arcsec with the unstrained lattice constants 0.5431 and 0.5658 nm for Si and Ge. In the XRD pattern of this study, the peak positions between Ge epilayers and Si wafer are larger than 5649 arcsec which indicates that the Ge epilayers are under compressive strain. We calculated the in-plane lattice constant (\( a_\parallel \)) of Ge epilayer as follows [22]:

\[
a_\parallel = \left( \frac{1 + \nu}{2\nu} \right) \left[ a_{Ge} - a_\perp \left( \frac{1 - \nu}{1 + \nu} \right) \right],
\]

where \( \nu \) is Poisson’s ratio of Ge, \( \nu = 0.271 \), \( a_{Ge} \) is the relaxed Ge lattice constant, \( a_{Ge} = 0.5658 \) nm, and \( a_\perp \) is the out-of-plane lattice constant of Ge epilayer calculated by Bragg’s law. Then, the residual strain of Ge epilayer can be estimated using [22] as follows:

\[
\text{Strain} = \frac{a_\parallel - a_{Ge}}{a_{Ge}},
\]

and the compressive strain values of Ge epilayers grown by various working pressure are shown in Figure 7; the compressive strain can be relaxed from 0.30 to 0.12% by increasing the working pressure from 15 to 30 mTorr.

In addition to the XRD patterns, we found that, in Raman spectra, the peak positions of Ge TO mode of Ge epilayers on Si shifted to larger wavenumber when the growth condition is at lower working pressure compared with a c-Ge wafer (300.90 cm\(^{-1}\)). The peak position shifted to larger wavenumber indicating the compressive strain in Ge epilayer. We also estimated the compressive strain by empirical expression [36]:

\[
\text{Strain} = \frac{\omega - \omega_{Ge}}{400},
\]

where \( \omega \) is the peak position of Ge TO mode and \( \omega_{Ge} \) is the peak position of a c-Ge wafer. The variation of compressive strain in Ge epilayers calculated by Raman spectra is also shown in Figure 7. We found that whether the compressive strain calculated by XRD or Raman, by increasing the working pressure to deposit the Ge epilayer on Si.

Different from the Ge epilayer grown on Si by high temperature process like MBE, UHV-CVD, or RPCVD, ECR-CVD can grow a Ge epilayer on Si at a low temperature of 180°C. For the Ge epilayer grown on Si by high temperature process, at the growth temperature, the Ge layer should be relaxed. However, during the cooling from high temperature to room temperature, a tensile strain is induced in Ge due to the mismatch of thermal expansion coefficient [8]. The thick Si substrate with a smaller thermal expansion coefficient prevents the lattice shrinkage of Ge during the cooling, leading to the generation of tensile strain in Ge. Therefore, the Ge epilayer (004) peak position will shift to larger diffraction angles. In this study, the ultralow temperature process leads the Ge epilayer under compressive strain. In order to relax the compressive strain in Ge layer, the postannealing process is usually used. However, the annealing process needs temperature above 400°C, such a high temperature will limit its application in devices or systems. In this study, we can use ECR-CVD direct grow the Ge epilayer on Si and by increasing...
the working pressure, the improvement of crystal quality and reduction of compress strain in Ge layer can be achieved.

We have used SE, XRD, and Raman measurement to identify the crystal quality of Ge epilayer and demonstrate that when the working pressure increased from 15 to 30 mTorr the crystal quality can be improved. To further observe the structural details of the film, we used cross sectional TEM to observe the epitaxial quality of the Ge/Si interface of the film shown in Figure 8 grown under 30 mTorr. As can be seen, it is clear that the Ge epilayer on the c-Si substrate is epitaxial. Besides the TEM micrograph, the surface morphology which is an important factor in device manufacture is also measured by AFM. A smooth surface can enhance the structural and electrical properties and reduce defects at the interface of devices such as photodetectors and solar cells because a better interface between different layers can reduce the carrier recombination effect. In the growth of Ge on Si films, the formation of a rough surface is mainly due to the dislocations threading up to the surface, the strain in the film [21, 37], and the Straniski-Krastanov growth mechanism [8]. Figure 9 shows the surface morphology of a 40 nm Ge epilayer on Si when the working pressure is 30 mTorr. The RMS surface roughness of the film is 0.342 nm and verifies that the Ge film deposited by ECR-CVD has an epitaxial structure with a flat surface which is beneficial to further device processing.

In addition to the crystal qualities identified by XRD, Raman, AFM, and TEM, we also used the Hall measurement to characterize the carrier concentration and mobility shown in Figure 10. For the Ge on Si, the defects in the epilayer will trap the electrons resulting the film to have a spontaneous p-type quality [38]. Therefore, the carrier concentration in the film can be used to represent the defects in the epilayer. When the working pressure increased from 15 to 30 mTorr, the concentration decreased from $1.03 \times 10^{18}$ to $6.5 \times 10^{17} \text{ cm}^{-3}$ which implies that the defect density in the film can be reduced. For the mobility, it is much related to the crystal qualities of Ge, and the increase of working pressure can improve the film qualities demonstrated by XRD and Raman, so that the highest mobility of 1163 cm$^2$/V can be obtained at the working pressure, 30 mTorr.

The Ge on Si has been used for developing optoelectronic components such as infrared photodetectors, lasers, and solar cells. The thin Ge epilayer (40 nm) on Si with flatten surface in this study is suitable to be a buffer layer between the III-V materials (GaInP, GaAs, or AlGaAs) and Si to develop the low cost and high efficiency III-V/Si tandem solar cells in our opinion. The Ge on Si can solve the lattice mismatch between III-V materials and Si. Moreover, the thin-thickness and smooth surface of Ge is necessary for the high efficiency III-V/Si tandem solar cell to reduce the optical loss in Ge buffer layer and recombination centers in the interface [29]. For the electron properties, the thin Ge epilayer has a high mobility 1163 cm$^2$/V indicating that the carrier can transport easily to prevent the recombination in the buffer layer.
4. Conclusions

Using a low temperature process cannot only decrease costs but can also reduce the restriction of high temperature processes on device manufacturing. In conclusion, we have successfully deposited flat and thin Ge epilayers directly on c-Si substrates under a low temperature of 180°C using ECR-CVD which is distinct from UHV-CVD, MBE, RPCVD, LEP-ECVD, or thermal vapor deposition methods with high-temperature processes. The results presented above demonstrate that, with the increase of working pressure, the structural quality of the Ge (004) epilayer can be better improved because of the higher dissociation identified by Ge⁺/GeH⁺ ratio measured by OES. When the working pressure is 30 mTorr, the Ge (004) FWHM in XRD is 683 arcsec, compressive strain in Ge epilayer is 0.12%, and the RMS surface roughness is 0.342 nm. An ordered Ge/Si interface under TEM measurement can be obtained demonstrating the epitaxial growth. For the electrical properties, the thin Ge epilayer has a high mobility of 1163 cm²/Vs indicating that the carrier can transport easily to reduce the recombination in the buffer layer. This indicates that ECR-CVD can be another choice for growing epitaxial Ge on Si. The thin-thickness and smooth surface of Ge epilayer grown on Si in this study is suitable to be a virtual substrate for developing the III-V devices including lasers, photodetectors, and low cost and high efficiency III-V/Si tandem solar cells in our opinion.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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