MeV ion-induced strain at nanoisland-semiconductor surface and interfaces

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Abstract

Strain at surfaces and interfaces play an important role in the optical and electronic properties of materials. MeV ion-induced strain determination in single crystal silicon substrates and in Ag (nanoisland)/Si(111) at surface and interfaces has been carried out using transmission electron microscopy (TEM) and surface-sensitive X-ray diffraction. Ag nanoislands are grown under various surface treatments using thermal evaporation in high vacuum conditions. Irradiation has been carried out with 1.5 MeV Au$^{2+}$ ions at various fluences and impact angles. Selected area electron diffraction (SAED) and lattice imaging (using TEM) has been used to determine the strain at surface and interfaces. Preliminary results on the use of surface-sensitive asymmetric x-ray Bragg reflection method have been discussed. The TEM results directly indicate a contraction in the silicon lattice due to ion-induced effects. The nanoislands have shadowed the ion beam resulting in lesser strain beneath the island structures in silicon substrates. High-resolution lattice imaging has also been used to determine the strain in around amorphization zones caused by the ion irradiation.

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1 Introduction

Lattice strain at surface and interfaces plays an important role in the structural evolution of many material systems. Lattice strain may be caused by lattice defects or heteroepitaxy or other kind of stresses. Knowing the strain distribution would result in tailoring the optical and electrical properties like the materials used in band gap engineering. In III-V compound semiconductors the strain is very sensitive to the composition of two semiconductor layers and band gap can be tailored by varying the strain between the layers \[1\]. The coherent island growth in the epitaxial film growth (known as S-K growth mode) is known to be due to the strain relaxation in the growing film after an initial wetting layer \[2\]. Hence, the degree of strain relaxation could be one of the main governing factors in coherent island growth. Strain measurement for individual islands would help to understand the coherent island growth mechanisms \[3\]. In electronic device technology, the presence of localized stress fields at the perimeter of the components of an integrated circuit found to play a negative role in obtaining the required device characteristics \[4\]. A. Armigliato et al., reported strain determination in silicon-based submicrometric electron devices using electron microscopy methods \[5\]. Recently, it was shown about the possibility of replicating nanostructures on silicon by low energy ion beams by etching amorphized zones that were not shadowed by nanostructures during ion beam irradiation \[6\].

In general, strain measurements are carried out by X-ray diffraction (XRD), transmission electron diffraction (TED) and Rutherford backscattering spectrometry/channeling (RBS/C) methods. These experimental techniques measure the strain values averaged over length scales from sub-microns to few hundred of microns. It is possible to get from the smaller length scales (in nanometer scales) by using special geometries and conditions in the above experimental methods. For example, it is possible to limit the penetration of x-rays by using grazing incidence methods or using RBS/C in glancing angle geometry. It is also possible to get strain in specific locations using nanobeam diffraction (NBD in TEM) or convergent beam diffraction (CBED in TEM) or lattice imaging (HRTEM).

Among the X-ray methods, high resolution XRD or rocking curves is a common method to determine the strain distribution in single crystalline samples. The strain component is derived by simulating the rocking curves with a model distribution of strains and by using dynamical theory formalism based on Takagi-Toupin formalism \[7\]. The rocking curve measurements have been carried out in grazing incidence geometry so as to make the method surface-sensitive. Using this technique, known as asymmetric Bragg-rocking curves, one can quantitatively determine the strain by measuring the bulk
reflection under the grazing conditions \cite{8, 9, 10, 11}. T. Emoto et al., determined the strain due to nickel diffusion into hydrogen-terminated Si(111) surface using this method \cite{10}. Kishino et al., \cite{11} extended the dynamical diffraction theory derived by Battermann and Cole \cite{12} to the case of grazing incidence. Hasegawa et al., found the width of the rocking curve for (311) reflection depends on the width of the oxide layer thickness and reported strain field distribution at SiO$_2$/Si(001) interface using the asymmetric Bragg reflection method \cite{13}. The x-ray methods are useful when the specimen under study remains mostly crystalline. The aforementioned X-ray methods give the information on integrated signal through the depth along which X-rays have penetrated. Similarly, Rutherford backscattering spectrometry/Channeling (RBS/C) is method to measure tetragonal strain in the single crystalline systems. The RBS/C methods has been used to determine the tetragonal strain at CoSi$_2$/Si(111) interface by using axial channeling conditions. Previously, by combining HRXRD (which was used to determine the strain component perpendicular to the surface normal) and RBS/C (which was used to determine the tetragonal strain), the in-plane strain component at CoSi$_2$/Si(111) interface had been obtained \cite{14}. RBS/C experimental method also represents an integrated strain component.

Using TEM, both imaging mode (i.e., image contrast and lattice imaging) and diffraction mode (selected area diffraction (SAD), nano-beam diffraction (NBD) and large angle convergent beam diffraction (CBED)) have been exploited for the strain determination \cite{3, 5, 15, 16, 17, 18, 19, 20}. The strain was measured by comparing the image contrast predicted by the numerically integrated two-beam Howie-Whelan equations with the two-beam diffraction contrast images of strained copper matrix with coherent cobalt inclusions \cite{15}. The strain measurements on quantum dots have been relied upon strain simulations using finite element analysis (FE) due to lack of existence analytical strain models \cite{16}. Recently, a quantitative characterization of size, shape and the strain of a coherent island in semiconductor heterostructures have been determined by using bright-field suppressed diffraction imaging condition for planar-section specimen \cite{3, 17}. Strains in crystals with amorphous surface films have been studied by using CBED and HRTEM experimental methods \cite{18}. Y. Androussi et al., reported the usefulness of fringe spacing in Moire-like fringes in TEM images to determine the strain field at the apex of coherently strained islands and mean composition of the island \cite{19}. A. Armigliato et al. used the CBED technique, for strain determination in silicon-based submicrometric electron devices \cite{5}.

For last few decades in the fabrication process of integrated circuit devices, ion implantation doping has become a primary step. The initial technological driving force for MeV ion implantation was to form a deep conducting
layer in silicon. There had been several studies reporting on the MeV ion-beam-induced damage studies in single crystal silicon [21, 22, 23]. Energetic ions induce damage in the silicon at higher fluences, a phase transformation from crystalline Si (c-Si) to amorphous Si (a-Si) can occur. Damage induced by ion irradiation in Si depends on fluence, flux, energy, mass of the ion, target temperature, impact angle etc. Understanding the amorphization process is still an active area of research and various mechanisms have been put forward [24]. J. Kamila et al., reported that onset of amorphization due to MeV Au ion implantation in silicon occurs at lower fluence for low incident ion currents [23]. It could be interesting to have a systematic study to determine the strain evolution in the progression of amorphization. Previous strain measurements for the cases of 160 keV O\(^+\) ion and 1 MeV O\(^+\) ion irradiation in silicon show negative strain [25, 26]. In this article, determination strain profile will be presented using HRTEM and asymmetric Bragg reflection methods.

Recently, a method of replicating nanostructures on Si surfaces using metal nanoparticles on Si as mask and low energy ion-irradiation has been proposed [6]. Accordingly, Si nanostructures produced on Si substrate have a one-to-one correspondence with the self-assembled metal (Ag, Au, Pt) nanoparticles initially grown on the substrate. The smallest structures of Si thus produced emit red light when exposed to UV light [6]. It is very important to understand the dominating factors for the amorphization process underneath the nanoislands. In this paper, shadowing effect of Ag nanoisland on the substrate silicon will be presented.

2 Experimental

The mirror polished (111) oriented Si single crystals were cleaned with de-ionized water followed by rinsing in methanol, trichloroethelene, methanol and a final rinse in de-ionized water. About 2.0 nm thick native oxide was present on the silicon surface. Implantations were carried out with 1.5 MeV Au\(^{2+}\) ions using 3.0 MV pelletron accelerator facility at Institute of Physics, Bhubaneswar. The implantation were carried out room temperature with an incident ion current \(\approx 20\) nA. To understand the shadowing effects of nanoparticles, isolated silver nanoislands were grown by depositing 2 nm thick Ag film on Si(111) surface using resistive heating method in high vacuum conditions and later, the ion irradiations were carried out at room temperature at various fluences and impact angles. The fluences on the samples were varied from \(1 \times 10^{12}\) to \(1 \times 10^{14}\) ions cm\(^{-2}\). The substrates were oriented 5° off normal to the incident beam to suppress the channeling effect for nor-
mal implantations ($0^\circ$). Cross-sectional Transmission Electron Microscopy (XTEM) observation was carried out using a 200 kV JEOL JEM 2010 (ultra high resolution mode) microscope for high resolution imaging. XTEM samples were prepared by a combination of mechanical polishing and followed by ion milling with 3.5 keV Ar$^+$ ions. ImageJ [27] is used to analyze the data. Surface sensitive asymmetric X-ray diffraction experiments were carried out in atmosphere at room temperature at beam line BL-15C at the Photon Factory of High Energy Accelerator Research Organization in Tsukuba, Japan [9]. For the observation of strain field near the substrate surface, the rocking curves of the (113) reflection of the substrate were measured. Since \{113\} planes are oriented at $\approx 29.5^\circ$ to \{111\} surface, the detector (NaI) was positioned at $\approx 59^\circ$ with respect to surface. The incident X-ray energy was tuned such that the measurements were done near the critical angle of total reflection (i.e., grazing incidence geometry).

3 Results and discussions

TEM measurements have been used to determine the strain quantitatively. Preliminary data using x-ray asymmetric Bragg-reflection has been presented. Two TEM modes: (i) selected area diffraction and (ii) lattice imaging have been used to determine the strain value from cross-section TEM specimen. The selected area electron diffraction (SAED) has been used with lowest aperture size (corresponding to $\approx 130$ nm at the specimen) at different depths before and after irradiation to determine the strain distribution along the depth of the target.

In general, the strain (in %) is defined as:

$$\varepsilon = \frac{d - d_0}{d_0} \times 100$$  \hspace{1cm} (1)

where $\varepsilon$ is the strain in percentage, $d$ and $d_0$ are the inter-planar spacing for strained and virgin specimen, Using $Dd = L\lambda$ (for diffraction in TEM), which can be written as

$$\varepsilon = \frac{D_0 - D}{D} \times 100$$  \hspace{1cm} (2)

where, D is the distance between the direct beam and diffracted beam for implanted sample (strained lattice) and $D_0$ is that of the virgin sample, L is the camera length and $\lambda$ is the wavelength of electron.

Figure 1(a) shows the XTEM bright field image of silicon after irradiation with 1.5 MeV Au$^{2+}$ at a fluence $5 \times 10^{13}$ ions cm$^{-2}$. Diffraction patterns from three selected areas corresponding to various depths have been taken:
surface, end of range (EOR) and bulk (un-irradiated part). The selected area at the specimen (SAED aperture corresponds to a region ≈ 130nm) at various depths corresponding to the above areas is show as circles with I, II and III legends inside the circles in the BF image. The respective diffraction pattern from surface (I), EOR (II) and bulk (III) have been shown in Figures 1(b), (c) and (d) respectively. From the SAED pattern, it is clear that a complete amorphization has not taken place even at EOR. It was shown in our previous work, the fluence required for amorphization was 1 × 10^{14} ions cm^{-2} [23]. Care had been taken to avoid the overlap of regions and alignment of aperture while taking SAED. The values of D and D_0 of both implanted and un-implanted (not shown) silicon have been determined. Strain in percent at different regions for different set of planes has been presented in Table 1. From the data of Table 1, it is clear that after the irradiation negative strain i.e., lattice contraction is induced in the system, similar to the work by S. L. Ellingboe et. al.,[26] at very high fluence compared to our work. At the EOR the strain is maximum for all set of planes and strain at surface is relatively weaker than other irradiated places. This is due to the damage and defect density at the EOR.

Table 1: Strain (%) at different depths of different set of planes for silicon irradiated with 1.5 MeV Au^{2+} at a fluence of 5 × 10^{13} ions cm^{-2} (Typical error in $\epsilon$ is < 1%)

| Set of planes | Strain at surface | Strain at EOR | Strain at Bulk |
|---------------|------------------|---------------|---------------|
| {002}         | -0.74            | -1.47         | -0.74         |
| {-111}        | -0.86            | -1.70         | -1.28         |
| {-11-1}       | -0.81            | -1.20         | -0.81         |
| {-220}        | 0.49             | -0.75         | -0.25         |

Figure 2(a) and (b) show the XTEM high-resolution bright field image at surface and EOR for post-irradiated Si with 1.5 MeV Au^{2+} at a fluence of 5 × 10^{13} ions cm^{-2}. It is clear from the figure that the surface after implantation remains crystalline. Previous results showed the amorphization to occur at 1 × 10^{14} ions cm^{-2} when the irradiation was carried out at an impact angle of 60° [23]. From the Figure 2(b), amorphous zones are present at EOR region. The interface of amorphous/ crystalline (a/c) is found to be sharp [28]. In this region, the d-spacing at various depths of the substrate has been measured from the lattice images. From the diffraction data, the strain is found to be maximum at EOR. We have found that the d spacing away from amorphous regions is same as that at the surface and differs compared to
the regions around amorphous zone. With the increase of fluence, the strain at the a/c interface found to increase and hence could result in amorphization at sufficient high fluence.

The figure 3(a) shows the XTEM bright field image of as deposited Ag nanoislands on Si(111) substrate. Figure 3(b) and 3(c) show the XTEM bright field image corresponds to with and without Ag nanoislands after the ion irradiation at a fluence of $1 \times 10^{13}$ ions cm$^{-2}$. In this case also, the strain has induced to the system after ion irradiation. Without Ag islands, the strain in Si surface is similar to that of Figure 2(a). But with the Ag islands, the strain in Si surface is found to be negligible and found to retain its crystalline structure even at larger fluences. That means the islands shadow the effect of irradiation on the surface. However the projected range of Au ions in Ag ($\approx 130$ nm calculated from TRIM [30]) much greater than the average height of the Ag islands ($\approx 17$ nm). So, in the same sample with Ag islands, amorphization would occur at higher fluence at different depths of the Si sample. The places without islands are getting amorphized at lower fluence due to lower strain values.

The experimental rocking curve obtained under asymmetric Bragg condition is shown (Figure 4) for virgin Si(111), 1.5 MeV Au$^{2+}$ ion implanted at 5° impact angle at a fluence of $5 \times 10^{12}$ and at fluence $5 \times 10^{13}$ ions cm$^{-2}$. From the Figure 4, the rocking curve from the irradiated specimen at a fluence of $5 \times 10^{13}$ ions cm$^{-2}$ is found to be asymmetric and show equally spaced satellite peaks. If it is assumed that these secondary peaks arises due to strain, then the maximum strain for the peak at extreme right show a maximum of 0.1% lattice contraction in $\{113\}$ inter-planar spacing. The appearance of oscillations (or satellite peaks) arises either due to strain or due to the presence of a very thin layer of different electron density from the substrate matrix. Simulations using modified Darwin theory and dynamical diffraction theory indicate broadening of rocking curve and appearance of satellite peak due to presence of compressive strain in the system [10]. A detailed analysis is under progress to understand x-ray data on various set of samples.

## 4 Conclusion

We have shown that strain can be determined along the depth by electron diffraction (SAED) and high resolution lattice imaging (HRTEM). TEM measurements show a compressive strain due to MeV ion implantation. Strain is found to be maximum at end of range (EOR) and relatively weaker at the surface. With the increase of fluence, the volume of amorphous zone is increased and the substrate tends to become amorphize from crystalline
structure. Ag nanoislands on the silicon substrate found to act as mask the underneath substrate resulting in retaining crystalline structure beneath the islands.

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Figure Captions

Figure 1: (a) TEM bright field image of 1.5 MeV Au\textsuperscript{2+} implanted Si(111) at a fluence of $5 \times 10^{13}$ cm\textsuperscript{-2} and (b), (c) and (d) are the SAED pattern of Si(111) from Surface, EOR and beyond EOR (bulk) respectively (corresponding regions I, II and III are depicted in the BF image).

Figure 2: HRTEM bright field image (a) at surface (b) at EOR of 1.5 MeV Au\textsuperscript{2+} implanted Si(111) with $5 \times 10^{13}$ cm\textsuperscript{-2}.

Figure 3: XTEM bright field image of (a) as deposited Ag islands and (b) with and (c) without island irradiated with 1.5 MeV Au\textsuperscript{2+} at a fluence $1 \times 10^{13}$ ions cm\textsuperscript{-2} on same sample.
Figure 4: Experimental X-ray data for asymmetric diffraction from (113) planes of single crystalline Si (virgin, 1.5 MeV Au ion irradiated at two fluences).
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