Research Article

Field Effect on Crystal Phase of Silicon in Si/CeO₂/SiO₂ Structure

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The structural, optical, and conductivity properties of silicon film deposited on cerium dioxide buffer layer were studied. The electronic structure of system consists of various defect levels inside band gap. The temperature spatial distribution plays a great role in silicon crystallization. The field destruction of crystal phase and its restoration, after annealing, were investigated.

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1. INTRODUCTION

In recent years, thin silicon films deposited on glass are widely used in various fields of electronic industry such as thin film transistors [1], integration circuits, photodetectors, and light-emitting devices. The main problem to improve parameters of electronic devices is the preparation of the crystalline homogenous thin film. However, the thin film (with thickness around 100 nm) deposition on glass substrate does not open possibility to check surely its properties, from one side, and to get crystalline material, from another side. In some instances, an amorphous film is deposited, and after annealing its crystallinity is improved. The other way is to deposit a buffer layer to prevent randomization in bonding by the deposition of silicon thin film on silicon oxide substrate. Cerium dioxide is a suitable dielectric ($E_{bg} = 5.5$ eV) with a crystal lattice parameter similar to silicon crystal structure to design the ultra-large-scale integration devices. Its dielectric constant is higher than 25, because by thin film transistors, making the leakage current for cerium dioxide thin dielectric layer with thickness of 2.8 nm is four orders of magnitude lower than ordinary SiO₂ dielectric layer [2] at an applied bias of 2 V.

In our work, we studied the field-stimulated destruction of crystal phase in silicon thin film deposited on ultrathin layer of cerium dioxide, and the recrystallization by annealing. The results of this research work can be

applied to memory devices design and creation of silicon cluster structures inside amorphous phase, including silicon nanowires. It is seen that only the silicon bonding as crystal structure can be made easily by preparing the preliminary temperature field of substrate. In this case, we can easily obtain the fine crystal structures on glass substrate with significant density of packaging for integration circuit. In addition, such crystal structure can be easily destroyed and restored because of memory effect.

Due to the possibility of large area deposition of thin silicon film on glass, we can achieve the large amount of elements in one unit. The magnetron sputtering of cerium dioxide combined with plasma-enhanced chemical vapor deposition (PECVD) technique results in potential industrial application of product.

2. EXPERIMENTS

2.1. Film preparation

Thin silicon film was deposited by using PECVD method. The gas mixture of silane and hydrogen was used. The temperature of deposition was in the range of 480–570 K. The buffer layer of cerium oxide was deposited on glass directly by using magnetron sputtering system. Its thickness was varied from 1 to 10 nm. Figure 1 shows the Raman spectrum of silicon film deposited on CeO₂ buffer layer. The

FIGURE 1: Raman spectrum of silicon film deposited on cerium oxide buffer layer with thickness of 1 nm.

FIGURE 3: Raman spectrum of silicon film by electric field applying. There is only amorphous phase, and no crystal. Crystal silicon bonding was destructed.

FIGURE 2: Scanning electron microscope data of silicon film (thickness being around 80 nm) deposited on cerium oxide layer and glass substrate (Corning 1737).

FIGURE 4: Raman spectrum of silicon film after 30-minute annealing at a temperature of 473 K.

measurements were done by means of probe Ar laser beam with wavelength of 488 nm, and were detected by double monochromator (Jobin Ivon, Kyoto, Japan) coupled with photo multiplier tube.

3. FIELD EFFECT ON SILICON FILM

3.1. Raman spectra

Figure 2 shows the scanning electron microscopic photo of silicon film deposited on glass substrate with buffer CeO_2 thin layer. Also, we studied the Raman spectra (Figure 3) by applying the electrical field 3–6 $\mu\text{V}/\text{\AA}$. It is seen that the crystal phase-related peak with position around 520 cm^{-1} has disappeared.

By annealing the sample with silicon film deposited on cerium dioxide layer, we obtained Raman data on the appearance of crystalline-related spectral peak around 520 cm^{-1} (see Figure 4), which were measured without application of external electric field. Silicon film was annealed in 30 minutes at a temperature of 473 K. The Raman scattering at elevated temperatures can be explained by quantum Raman susceptibility [3].

3.2. Conductivity measurements

Conductivity measurements as a function of annealing temperature are shown in Figure 5. The silicon film deposited on Corning 7059 substrate has activation energy of 0.2 eV and high value of conductivity due to the high concentration of defects and high crystallinity. The lower conductivity corresponds to the silicon film deposited on thin buffer layer of cerium dioxide because of low content of crystal phase ($E_{bg} = 1.12$ eV) and high fraction of amorphous phase with energy band gap of $E_{bg} = 1.77$ eV.

3.3. Local factors on micro- and nanoscales

The equations for local factors determination on nanoscopic and microscopic scales are strictly different. For microscopic scale, the dipole local field factors surrounding is significant as for nonlinear [4] as well as linear optical response:

$$L(\omega, \rho) = \frac{\rho}{4\pi} \frac{(\epsilon_c(\omega) - \epsilon_a(\omega))}{1 + (\epsilon_c(\omega) - \epsilon_a(\omega))(\Lambda - \beta\rho)}, \quad (1)$$

where ϵ_c and ϵ_a are dielectric functions of crystalline and amorphous silicon, respectively. For sphere depolarization

FIGURE 5: Conductivity measurements of silicon films deposited on glass substrates, Corning 7059 and Corning 1737, with cerium oxide buffer layer of 1 nm.

factor Λ is equal to $1/3$, β is the Lorentz constant ($\beta = 1/3$ for a homogeneous spherical surrounding).

The crystal phase homogeneity on the microscope is low, compared to silicon films with large thickness. The crystallization of silicon here mainly depends on the crystallization of cerium dioxide layer. Figure 6 shows the Raman spectrum for silicon film deposited on cerium dioxide buffer layer by high-temperature (600°C) conditions. It is seen that the crystal phase-related spectral peak around 520 cm^{-1} and wide spectra peak extended from 440 cm^{-1} to 500 cm^{-1} . The spectral deconvolution illustrates eight main oscillators with defined eigenfrequencies. One of them with position 456 cm^{-1} is related to the Ce–O dipoles. Silicon nanocrystal bonds that are weaker than bulk crystal bonding cause the spectral peak around 500 cm^{-1} .

For nanoscopic scale, the local field factor (see Figure 8) is determined by tensor of polarizability [5]. Dielectric susceptibility tensor can be written as

$$\chi_{\alpha\beta} = \partial P_\alpha / \partial E_\beta, \quad (2)$$

where P_α is the component of polarization along the Cartesian coordinates, and E_β is the component of external field. The film polarization mainly contributed to various components of dipole moments along the coordinates, particularly the dipoles Si–O–Si on film surface and intergrains boundary. We can estimate the value of dipole moment by the angle between the two Si–O bonds being around 90° using formula for quantum dipole:

$$\begin{aligned} \mu^{\text{Si-O-Si}}_{2\text{pO-3pSi}} \\ = 2\sqrt{2}\pi e \int_0^\xi \int_0^{2\pi} \int_0^\pi \Psi_{3p_x\text{Si}} \Psi_{3p_y\text{Si}} r \Psi_{2p_x\text{-O}} \Psi_{2p_y\text{-O}} r^2 dr d\varphi d\theta. \end{aligned} \quad (3)$$

FIGURE 6: Raman spectrum deconvoluted by using Gauss and Lorentz peaks. The Ce–O bonding is a related $456\text{--}460\text{ cm}^{-1}$ spectral peak.

The dipole moment is equal to the 1.4 D . The orientation of dipoles inside silicon film plays a great role in optical response because of strong asymmetrical properties and sufficient polarization charge. It is necessary to note that the electron wave function in Si–O–Si configuration is distributed among the 12 silicon atoms [6], because, to calculate the tensor value for Si/CeO₂/SiO₂ structure for thin silicon film, we can use the linear combination of all components along the coordinates:

$$\begin{aligned} \chi^{\text{Silicon-film}}_{\text{Si-O Intergrain}}^{(1)} &= \chi^{\text{Si-O Intergrain}}_{\text{Si-O Intergrain}}^{(1)} + \chi^{\text{film-surface}}_{\text{film-surface}}^{(1)} \\ &+ \chi^{\text{CeO-Si Interface}}_{\text{CeO-Si Interface}}^{(1)}. \end{aligned} \quad (4)$$

Figure 7 shows the microscopic homogeneity of crystal phase for silicon film. The crystal phase is inhomogeneously laterally distributed according to surface temperature fields' variations. Figure 8 illustrates the morphology of silicon film surface. It is clear that using dipole-surrounding calculations can combine the local factor field. The Si–O bonding on silicon film surface plays a great role in local factor value determination. For more detailed description to calculate local factor field value, we use the silicon nanocrystal orientation, oxygen atoms incorporation on silicon surface, as well.

4. MODEL OF FIELD DESTRUCTION

4.1. Silicon clusters and nanowires

The structural properties of silicon film deposited on crystalline buffer layer of cerium dioxide strictly depend on the cerium dioxide crystallinity lateral distribution. The cerium dioxide nanocrystals are deposited by magnetron target sputtering at determined temperature of substrate. Increasing the temperature of substrate causes the increase in cerium dioxide nanocrystal lateral density, because, by using the definite silicon film preparation, the appearance of silicon crystal nanostructures with single bonding is observed. Such single-bonding one-dimensional structure can extend through the silicon film. Silicon nanoclusters and nanowires made by applying nanoscopic temperature field consist of

FIGURE 7: Raman mapping measurements of silicon crystal phase for silicon film deposited on CeO_2 buffer layer. Thickness of buffer layer is 90 nm.

FIGURE 8: The microscopic photo of silicon film.

silicon bonding with surely one-dimension scale. The field-stimulated destruction can only be achieved by silicon-silicon bond elimination and defect creation such as dangling bond. The memory effect for nanostructured silicon crystals can be observed by annealing the $\text{Si}/\text{CeO}_2/\text{SiO}_2$ structure. It is clear that the appearance of crystal phase every time by annealing depends on the minimums of potential energy that are determined by cerium dioxide nanocrystals' spatial positions.

4.2. Oxygen incorporated into Silicon

For thin silicon films (thickness being less than 100 nm) deposited on silicon oxide, the concentration of oxygen atoms is significant. Usually, the oxygen atoms are incorporated with silicon in grain boundary of nanocrystals by complicated surface morphology of film, because the proposed model [7] of stabilized silicon-oxygen incorporation in the

grain boundary after transformation of the silanol groups into strong siloxane bonds was calculated for two types of structures: 13 silicon atoms incorporated with 14 atoms of oxygen (SiO_x , $x \approx 1$) by the Si–O bond angle being equal to 130° , the size of glass cluster is around $8.86 \text{ \AA}$; 29 silicon atoms incorporated with 39 oxygen atoms ($x \approx 1.34$) create the glass cluster size being equal to $14.77 \text{ \AA}$. The consequence of the saddle points in potential energy of oxygen atom was changed by the stress [8].

4.3. Role of cerium dioxide

For the silicon crystallization in thin silicon film, the role of crystallized clusters of cerium dioxide is great. The crystallization conditions of cerium oxide layer are different from the silicon film deposition conditions. Because of the high temperature of cerium silicide creation, we suppose that the main role in silicon crystallization is played by a temperature field on substrate.

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