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主　論　文　の　要　旨

論文題目　**Role of impurity deposition in the formation of silicon nanocone by using low energy helium plasma irradiation (低エネルギーヘリウムプラズマ照射によるシリコンナノコーンの形成における不純物堆積の役割)**

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論　文　内　容　の　要　旨

The purpose of this study is to understand the mechanism of silicon (Si) nanocones formation by low energy plasma irradiation and discuss how to control the characteristics of nanocone morphology by experimental conditions. Si nanocones were formed by low energy He plasma irradiation with different sample temperature, He ion fluence, and species of impurity seed, so as to find out the main factors which influence the Si surface morphology. Real sputtering yields for different morphology of Si-NCs have been calculated via the erosion depth and compared with value on a flat surface. The mechanism of low energy plasma-induced Si-NCs formation was elementarily discussed. In order to verify the hypothetical mechanism, a Monte Carlo simulation code was applied to simulate the formation of Si nanocones. Growth of nanocone under the ion bombardment in both vertical and tilted direction was compared with the phenomena observed in experiments. Line-of-sight redeposition effect of Si was involved in the simulation. Moreover, design of experiment was improved in a more controllable manner. Parameters which significantly change the Si surface morphology can be quantified. It revealed the relation between experimental parameters and features of Si-NCs. By comparing the energy dispersive X-ray spectrometer (EDX) mapping result of nanocones with different features, a model that illustrate the process of nanocone formation was build up. The relation between optical reflection of the irradiated surface and features of Si nanocones was also discussed.

In chapter 1, nanocone surface morphology which can improve the performance of materials to relief issues of energy crisis and global warming have been introduced. The importance and application of Si nanocones have been addressed. Conventional methods to fabricate Si nanocones were introduced, as well as a relative novel method, low energy plasma irradiation. Advantages and the unsolved issues of plasma irradiation method have been pointed out. Finally, the purpose of this thesis was presented.

Chapter 2 introduced the experiment device, Co-NAGDIS, which was utilized in this study. Schematic of the overall device design and the sample irradiation position have been presented. Typical experimental condition was introduced including back ground pressure, neutral gas pressure during the plasma irradiation, magnetic field, electron temperature, and electron density. The measurement of plasma parameters was done by single Langmuir probe. The principle of Langmuir probe was introduced to illustrate the calculation of electron temperature, density, and ion flux. Besides, SURO (abbreviated from SUface ROughness) is the code which was applied in the numerical work presented in chapter 4. The flow of how SURO works was described schematically. Sputtering, which is one of the most important processes of the Si nanocone formation as well as the simulation, have been detailed. SURO code is based on Monte Carlo method. This method was briefly introduced for a better understanding of the code.

In chapter 3, Si samples were exposed in He plasma. Two typical surface morphologies have been observed on Si surfaces by a scanning electron microscope (SEM): small (~0.01 μm^2) and high density of nanocones with low (~2%) optical reflectance (black Si), and large (~0.1 μm^2) and low density nanocones with relatively high (~40%) optical reflectance (white Si). After the surface analyzation by X-ray photoelectron spectroscopy (XPS), amount of impurities which deposit on the surface is the key factor which cause the different morphology. A large amount of impurities lead to the formation of black Si. The real sputtering yield, calculated via the erosion depth, of black Si was less than half of that of white Si. This indicated that the formation of nanocones is attribute to the shielding effect of deposited molybdenum (Mo) impurities during the ion bombardment. Observations on nanocone through transmission election microscope (TEM) revealed that low energy He plasma irradiation remains the Si nanocones and the substrate good crystalline structure.

In chapter 4, a numerical work has been developed with SURO code based on the energy dispersive spectroscopy (EDS) mapping result on a single Si nanocone to concrete the theory above. The formation process of the nanocone from a flat surface was presented. The modeling structure under an inclining ion incident direction was in good agreement with the experimental result. Moreover, the redeposition effect due to the line-of-sight was proposed as another important process of nanocone formation based on results from the comparison of the cone diameter and sputtering yield between cases with and without the redeposition effect. The redeposition effect will enlarge the diameter of the cone. It could be the reason for the gentle decrease of the sputtering yield during the long period of irradiation. Increasing of the density of nanocone on the simulation region enhanced this redeposition effect.

In chapter 5, a biased Mo sputtering wire was introduced in front of the Si substrate during the plasma irradiation. Uniform black Si can be easily obtained with this method at surface temperature of 500 °C and ion fluence of $2.5\times10^{25}\,\mathrm{m}^{-2}$. Mo impurity fluxes have been quantified through the intensity of the Mo emission light. Plasma irradiation experiments were conducted under different He ion energies on the sputtering wire E_{SW} and the Si substrate E_{Sub}. It was found that the averaged aspect ratio (height over diameter of cone) of nanocones has a linear dependence on the logarithm of Mo flux ratio. The slope of this linear dependence is almost constant at different E_{Sub}. The reason of this relationship is strongly related with the fraction of Mo on the upper region of the cone according to the observation in EDS for different aspect ratio cases. With the assistant of TEM images of a single nanocone, the high fraction of Mo was clearly identified as black dot on the tip of cone. Moreover, a layer on the side of the bottom of the cone with high transparency was observed. This layer had the same features as the redeposition layer founded in the simulation work above. Nanostructures on the irradiated surface were also compared between a full time Mo deposition case and a half time case. The usual cone structure shrunk to needle-like structure after the Mo deposition was cut off. This phenomenon indicated that protrusion on the Si surface without the coverage of Mo can be flattened again due to the angular dependence of sputtering yield. Besides, nanocones structure with the height larger than 400 nm and the diameter larger than 100 nm contribute to the suppression of reflection smaller than 2%.