Transactions of the Materials Research Society of Japan 27 [4] 815-818 (2002)

Deposition of Nanocrystalline Silicon Films Using High-Vacuum Silicon Evaporation with Oxygen and Argon Radicals

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Nanocrystalline silicon films were deposited on silicon substrates by evaporating elemental silicon in an ultra-high vacuum. Oxygen and argon radicals were introduced during silicon-evaporation in order to control the Si-Si and Si-O bonding in the deposited film. The films with the O_2 fraction of 100%, 50% and 20% in the introduced O_2 and Ar gas mixture were prepared in this work. The film thickness was decreased with decreasing the O_2 fraction. The silicon and oxygen composition in the deposited film was characterized by Rutherford backscattering spectrometry (RBS), which revealed that the uniform depth profile was obtained by introducing the Ar gas. The deposition mechanism was also discussed in terms of chemical bonding using X-ray photoelectron spectroscopy (XPS).

Key words: Nanocrystalline, Silicon, Radical, Oxygen, Argon

1. INTRODUCTION

Many efforts have been made in the study of nano-crystalline silicon since the observation of strong visible photoluminescence from porous silicon at room temperature.[1] Nanostructures are of great interest and have been intensively investigated from the viewpoint of both fundamental physics and device applications, because they induce various quantum phenomena.[2-6] Nanocrystalline silicon is expected as a visible light-emitting material for the application to optoelectronic integrated circuits (OEIC), where optical devices are combined with present silicon-IC. It was reported that silicon crystals could exhibit visible photoluminescence at room temperature when they were made very small.[7] In Ref. 7, photoluminescence with a peak energy of ~ 1.3 eV, which is much higher than the band gap for bulk silicon, was observed from ultrafine (2 ~ 5 nm in diameter) silicon particles. Furthermore, it was reported that the wavelength of the luminescence became shorter with decreasing the grain size.[8] In these reports, silicon particles were produced by means of microwave plasma decomposition of SiH_4, H_2 and Ar gas mixture[8] or a planar magnetron RF sputtering technique in H_2 gas.[7] Silicon-evaporation technique is not mainly used for the preparation of silicon nano-particles.

In this study, nanocrystalline silicon films were deposited by silicon-evaporation in an ultra-high vacuum with oxygen and argon radicals and the deposition mechanism was discussed.

2. EXPERIMENTAL PROCEDURE

Nanocrystalline silicon films were deposited in an

ultra-high vacuum MBE chamber evacuated by a turbo-molecular pump. The base pressure of the MBE chamber was about 5×10^{-10} Torr. Silicon (100) was used as a substrate. Prior to the film deposition, the substrates were cleaned in acetone, methanol and deionized water. They were also dipped in diluted HF solution in order to remove natural oxide on the surface of the substrates. High-purity silicon was evaporated by an electron-beam gun (3 kW) onto the substrate. The substrate temperature for the film deposition was 500℃. Oxygen and argon radicals were supplied during silicon-evaporation. Films with the O_2 fraction of 100%, 50% and 20% in the introduced O_2 and Ar gas mixture were prepared in this work. The total flow rate of the introduced O_2 and Ar gas mixture was 0.5 sccm and the RF power was 150 W. The chamber was held to a pressure of $10^{-6} \sim 10^{-7}$ Torr during the film deposition. The deposition time was 120 min for all cases. Figure 1 shows the schematic of the apparatus used for the deposition of nanocrystalline silicon films in this study.

The deposited silicon films were characterized by Rutherford backscattering spectrometry (RBS) and X-ray photoelectron spectroscopy (XPS). The thickness of the films was measured using a laser-probe microscope.

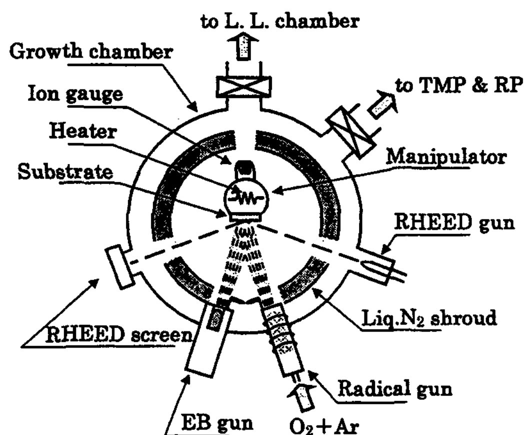
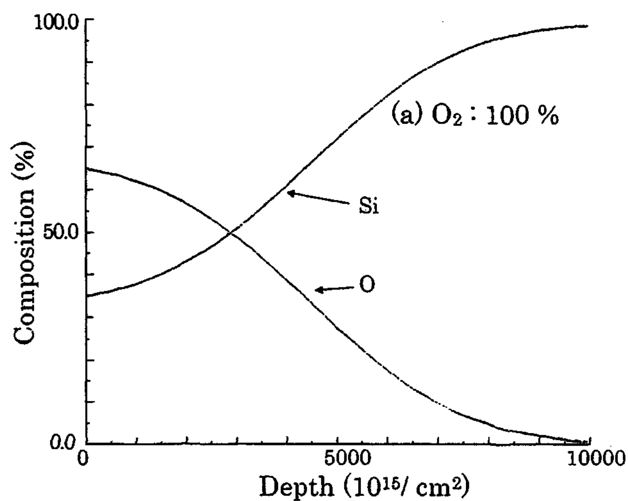


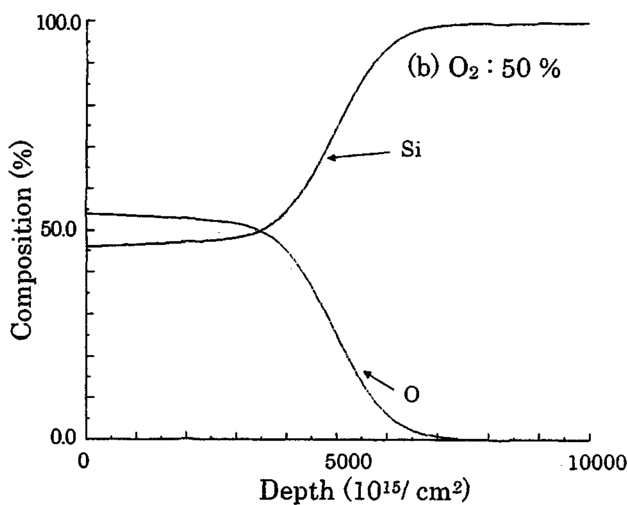
Fig.1 Schematic diagram of the apparatus used for the deposition of nanocrystalline silicon films.

3. RESULTS AND DISCUSSION

Figure 2 shows the depth profile of the silicon and oxygen atom composition obtained by RBS measurements with He ions at an energy of 2.0 MeV for the films prepared with O_2 fractions of (a) 100%, (b) 50% and (c) 20%. In Fig.2(a), silicon and oxygen atom composition changes gradually in the deposited film. When O_2 (100%) was introduced during deposition, the energy of the oxygen radicals reached to the substrate were relatively low and their number was small because O^+ and O_2^+ ions were eliminated by the ion trapper mounted at the top of the radical gun. Consequently, silicon was deposited mainly at the initial stage and the composition of oxygen atoms increased gradually. On the other hand, when argon was introduced together with oxygen, the oxygen radicals became more energetic and the number became larger because argon is effective to keep plasma in good condition. The reactive oxygen radicals having larger energies reacted with silicon atoms from the early stage of the deposition and formed SiO_x networks. Therefore, the atom composition in the film changed suddenly as seen in Fig.2(b) and (c). The film thickness became smaller when argon was introduced because of the bombardment effect of the argon ions.[9] When oxygen fraction was far more decreased, the film thickness became much smaller because the number of the argon ions became much larger.

Figure 3 shows the XPS spectra for the films prepared with O_2 fractions of (a) 100%, (b) 50% and (c) 20%. The chemical bonding state (Si-Si and Si-O_x) as a function of depth was studied using XPS each time a layer was removed from the film surface by argon ion-beam sputtering in the spectrometer chamber. In Fig.3(a), (b) and (c), each spectra from the top to the bottom represents the chemical bonding state at each position from surface of the deposited film to the interface between silicon substrate and the deposited film.





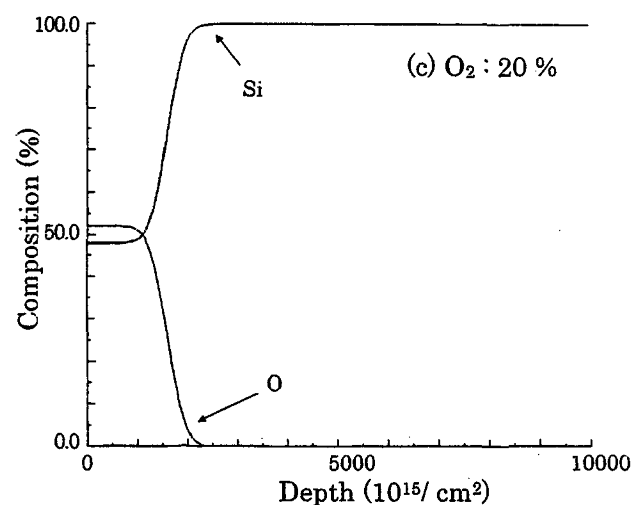
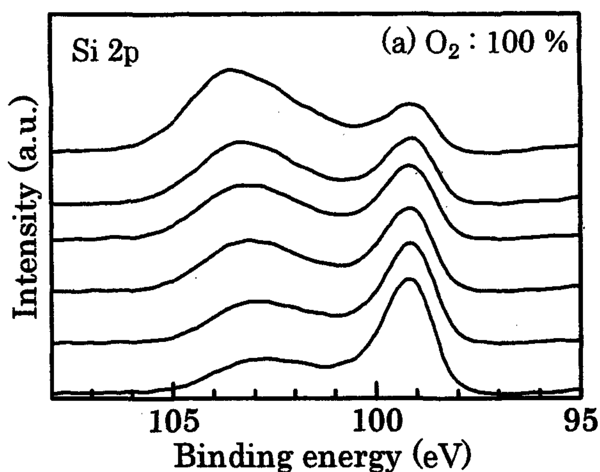
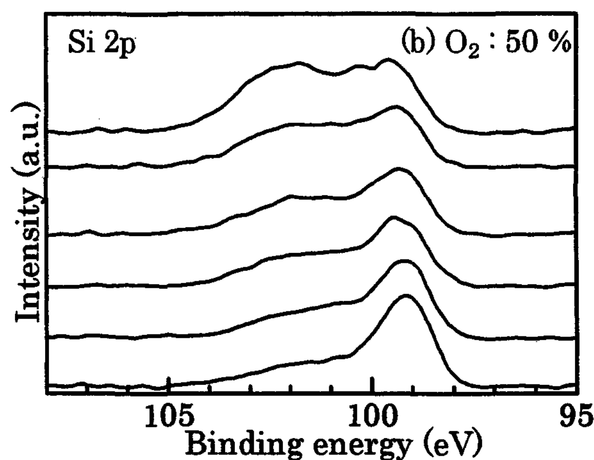


Fig.2 Depth profile of the silicon and oxygen atom composition obtained by RBS measurements for the films prepared with O_2 fractions of (a) 100%, (b) 50% and (c) 20%.





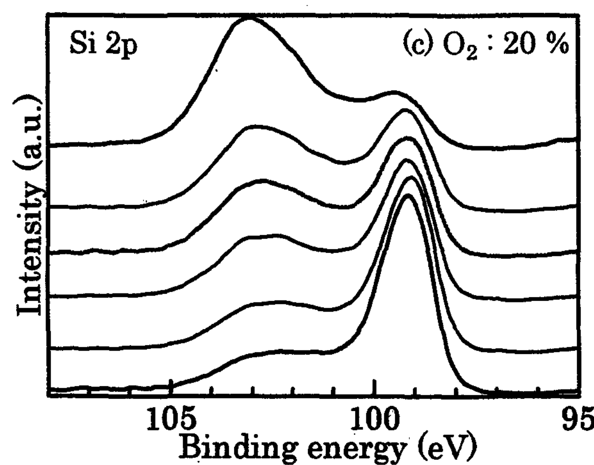


Fig.3 XPS spectra for the films prepared with O_2 fractions of (a) 100%, (b) 50% and (c) 20%. Each spectra from the top to the bottom represents the chemical bonding state at each position from surface of the deposited film to the interface between silicon substrate and the deposited film.

In Fig.3(b), that is when O_2 fraction was 50%, the peak indicating Si-O_2 bonding (~103 eV) was weak and Si-Si bonding (~99 eV) was still dominant even at the surface of the film. However, the peak indicating Si-O_2 bonding (~103 eV) exhibits a remarkable increase towards the surface of the film when O_2 fraction was 20% as shown in Fig.3(c). This may be explained as follows; when argon fraction was larger (Fig.3(c) compared to Fig.3(b)), more reactive oxygen radicals enhanced the oxidation of the film and Si-O_2 network was formed.

4. SUMMARY

Nanocrystalline silicon films were deposited on silicon substrates by evaporating elemental silicon in an ultra-high vacuum. Oxygen and argon radicals were introduced during silicon-evaporation in order to control the Si-Si and Si-O bonding in the deposited film. The films with the O_2 fraction of 100%, 50% and 20% in the introduced O_2 and Ar gas mixture were prepared in this work. The film thickness was decreased with decreasing the O_2 fraction. The silicon and oxygen composition in the deposited film was characterized by RBS, which revealed that the uniform depth profile was obtained by introducing the Ar gas. The deposition mechanism was also discussed in terms of chemical bonding using XPS.

ACKNOWLEDGEMENT

This work was financially supported by the Kansai University Grant-in-Aid for the Faculty Joint Research Program, 2001.

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(Received December 20, 2001; Accepted January 31, 2002)