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Studies of the TiO_2-Si Interface Bombarded by Ar^+ Ion Beam

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Abstract

It is experimentally shown that a TiO_2 film on Si(111) substrate was prepared by using the technique of D.C. reaction sputter deposition with Ar^+ ion beam bombardment, and a layer-like structure was observed from the depth profile of the interface between TiO_2 film and Si substrate with Scanning Electron Microscopy and Electron Probe. It was also surprisingly discovered that Ti atoms could be detected at about 9 μm depth. The TiO_2-Si interface bombarded by Ar^+ ion beams revealed multi-layer structures, a mechanism might be caused by defect diffusion, impurity and matrix relocation. Multi-relocations of impurity and matrix atoms were as a result of profile broadening of the TiO_2-Si interface, and the spread due to matrix relocation in this system is shown to exceed much more the spread due to impurity relocation.

Keywords : TiO_2-Si interface, Ar^+ ion beam bombardment, multi-layer structures, multi-relocations

1. Introduction

Man-made semiconductor nano-structures could revolutionize optoelectronic technology. The recent past has seen increased interest in the combination of size quantitative effects and interface phenomena [1]. It should be mentioned here that some interface phenomena are in general not considered in the study of quantum-sized semiconductors. Such as the depth profile of multi-layers was induced by cascade mixing and recoil implantation in solids by ion beam bombardment, concentration profiles being shifted and broadened with increasing ion beam flux. The possibility of a shift, although mentioned occasionally [2], received little attention from a quantitative point of view. Even the so called mixing-roughness-information (MRI) depth-model and its application to the quantitative reconstruction of the in-depth distribution of composition [3], with a typical accuracy of one monolayer and better, was demonstrated for SIMS and AES depth profiles, little is known about the relation of various long- and short-range mixing mechanisms.

In this contribution, we describe the study of the TiO_2-Si interface bombarded by Ar^+ ion beam. A widely irradiation-induced profile with layer-like structures was observed by Scanning Electron Microscopy and Electron Probe from the interface between TiO_2 film and Si substrate. We shall try to discuss several mechanisms which might explain the phenomenon observed in this experiment.

2. Experimental procedure

TiO_2 films on Si(111) substrate was prepared by using the technique of D.C. reaction sputter deposition with Ar^+ ion beam bombardment. The substrate of TiO_2 thin films was a wafer of clean single-crystal Si(111). The target material for sputtering was 99% Ti cleaned by Ar^+ sputtering before sample preparation. The argon

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and oxygen were used as sputtering atmosphere. The bass pressure was 2.1×10^{-5} Torr.

The process of preparing samples took the following three steps: TiO_2 films had first deposited on the Si surface for 20 minutes using D.C. reactive sputtering technique, the film thickness about 50 nm; secondly, the deposited TiO_2 layer on Si was perpendicularly bombarded with Ar^+ ion beam of 30 keV at 5×10^{16} cm^{-2} dose; finally, TiO_2 films had deposited again for 20 minutes in the same way of the first step.

The prepared sample was cleaved by force and the fresh profile was observed with SEM (HITACHI S-450). And then the sample was irradiated perpendicular to Si(111) surface by 2MeV neutrons to a dose of 10^{17}-10^{19} cm^{-2} and measured as a result of neutron irradiation with Electron Probe (SHIMADZU EMPA-8705Q).

3. Results and discussion

Fig. 1 shows a SEM image of the depth profile of the TiO_2-Si interface bombarded by Ar^+ ion beam. The bright line most close to the left in this figure is a TiO_2 film, its thickness about 42 nm, and the dark area most close to the right is a Si(111) substrate. A layer-like structure up to 10 μm width appeared at the interface between the TiO_2 film and Si substrate. From results of SEM measurement, all layers at the TiO_2-Si interface mainly consist of Si element, but the X-ray Peak/Background (P/B) of the Si substrate were stronger than that of bright layers. The more it closes to the substrate, the stronger the P/B of a dark layer is, and the X-ray intensity of Si element increases with depth in the TiO_2-Si interface. This suggests that both bright layers and dark layers might not be original silicon structures. A quantized depth distribution of composition might occur at the area between the TiO_2 film and Si substrate. It is demonstrated for our XPS and AES analysis [4]. The results show that the layer-like structure close to surface is formed by a mixed layer of cross-linking Ti-O-Si bonds and titanium oxides vary along with the film depth. The mixed layer consists of TiO_2, Ti_2O_3, TiO, partial oxidized SiO_2-x, pure silicon and other micro-impurity elements. Titanium enters the silicon substrate and silicon diffuses into the film during Ar^+ ion beam bombardment, which causes co-existence of various titanium oxides and the fraction of TiO_2 first gradually reduces and then increases with the film depth.

To obtain a more detailed understanding of the

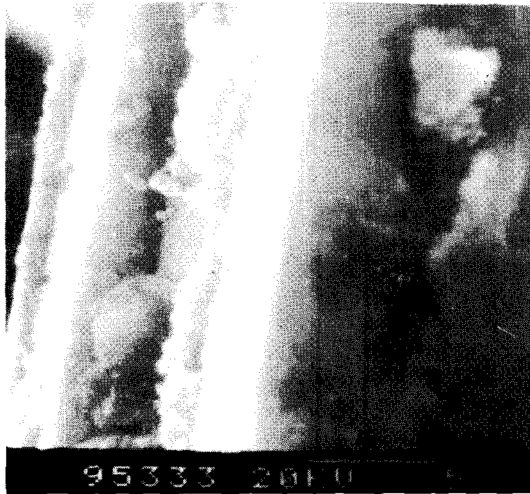

Fig. 1. SEM image of the depth profile at the interface between TiO_2 film and Si substrate.

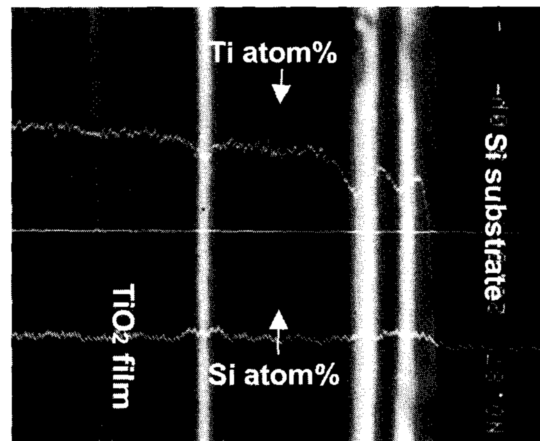

Fig. 2. Topography of the profile at the interface between TiO_2 films and Si substrate, both the upper and bottom curves show separately Si(atom%) and Ti(atom%) varying with the depth, which were obtained by Electron Probe.

TiO_2-Si interface with multi-layer structures, the sample in the Fig. 1 was irradiated by 2 MeV neutrons to a dose of 10^{17}-10^{19} cm^{-2} and measured for the depth profile of this sample with Electron Probe. It was found that the range of the TiO_2-Si interface was expanded over 20 μm and its original measured profile Fig. 1 changed into a new multi-layer structure see Fig. 2, and further data for each layer components were shown in Table. 1, where Sc element came from neutron irradiation of Ti atoms implanted into Si substrate. According to these data, it was found that bright layers included more impurity than dark layers, and different dark layers incorporated different components. Variations of the depth profile structure resulted from three movements due to neutron irradiation: cascades mixing, irradiation-enhanced diffusion, impurity and matrix relocation.

Table 1. Depth distributions of composition in the TiO_2-Si interface, achieved from the measured depth profile in Fig. 2 by means of Electron Probe.

Depth (μm)	Si (Atom%)	Ti (Atom%)	Sc (Atom%)	Layer Mark
	97	2.98	0.00	1st bright layer
	95	1.79	0.00	1st bright layer
	98	0.00	0.00	1st dark layer
	10	0.00	0.00	1st dark layer
	96	2.54	1.03	2nd bright layer
	98	0.00	1.05	2nd bright layer
	99	0.00	0.00	2nd dark layer
	99	0.17	0.00	2nd dark layer
	99	0.00	0.00	2nd dark layer
	10	0.00	0.00	2nd dark layer
	99	0.00	0.00	2nd dark layer
	10	0.00	0.00	2nd dark layer
	99	0.22	0.00	2nd dark layer
	10	0.00	0.00	2nd dark layer
	99	0.45	0.20	3rd bright layer
	99	0.00	0.10	3rd bright layer
	99	0.00	0.83	3rd bright layer
	10	0.00	0.00	Si substrate

Among of them, multi-relocations of impurity and matrix atoms were as a result of profile broadening of the TiO_2-Si interface, and the spread due to matrix relocation in this system is shown to exceed the spread due to impurity relocation by a factor of ~20 [5] and turns out to be in good agreement with our experimental results.

For the formation of layer-like structure profile in the TiO_2-Si interface, a fundamental mechanism is believed for it to be caused by defect diffusion, impurity and matrix relocation. Atom relocation from their lattice sites to other lattice sites is also a sort of damage occurring under ion bombardment, called ion-beam mixing. It is beneficial for thin-film adhesion in ion-assisted growth processes. Damage and atom relocation are less affected by channeling. The total numbers of defects created and of relocated atoms depend only slightly on the ion-beam incidence angle [6], but a slight shift of the layer-like structure profiles appeared in the beam direction.

4. Conclusions

The TiO_2-Si interface bombarded by Ar^+ ion beams and additional subsequent neutrons appeared multi-layer structures. Different layers incorporated different micro-impurity elements and components. The mechanism of quantizing structures might be caused by defect diffusion, impurity and matrix relocation. Multi-relocations of impurity and matrix atoms let to the profile broadening of TiO_2-Si interface, and the spread due to matrix relocation in this system is shown to exceed the spread due to impurity relocation about 20 times.

Acknowledgements

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