技術資料

Development of Standard Materials for Surface Analysis in KRISS

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1. Introduction

As the semiconductor industries and other advanced technology industries grow so fast, new materials of various thin films have been developed and applied to many fields. Because of this, the accurate and detailed information on the chemical composition, the depth profiles of elements, and the chemical state of constituents of thin films become very important recently. In order to obtain such information, international co-operations(VAMAS-Surface Chemical Analysis, ISO) pursue the standardization of surface analysis as well as the innovations and refinements of surface analysis techniques.

For the standardization of surface analysis, the absolute quantitative analysis should be accomplished. Up to now, however, this is very difficult because the data obtained by the conventional analysis techniques vary depending upon the pre-treatment methods of samples, the sample status as well as the technique itself. Therefore, the development of standard materials helps to solve those problems and to compare the data by each technique. The basic procedures for the determination of the standard materials are in three ways; 1. Preparation of the well-designed sample, 2. Analysis of the sample with various techniques to quantify it, 3. Comparison the data obtained by different instruments (RRT).

In KRISS, we are developing several standard materials for surface analysis using ion beam sputter deposition and ion implantation techniques. Those materials are for the depth profiling and the quantitative surface analysis. Various techniques are used to certified the standard materials.

2. Sample preparation and analysis

(1) Multilayer samples for the depth profile by SIMS

The standard materials for the depth profile require the characteristics of the homogenous distribution of elements in the whole layer, the well-defined surface and the interface of the film. And also the surface should not be modified severely during the ion bombardment.

The home-made apparatus for multilayer thin films are consisted of vacuum pumps and chamber, DC Ar ion gun for target sputtering, RF ion gun for deposition assistance, inlet gas monitoring devices, sample transportation system, and target and substrate holder. Through cooling water, the target temperature is sustained at the constant temperature. With the linear and rotary motion feed-through, the substrate can be set at the specified position and be rotated during the deposition to form a uniform thickness of thin film. The thickness is controlled by the commercial deposition monitor (INFICON; XTM/2) initially, and then with the constant conditions, controlling the deposition time is good enough to get a specified thickness. In Fig. 1, the schematic drawing of the apparatus is presented.

The ion beam sputter deposition (IBSD) has several advantages over the conventional RF magnetron sputtering: 1) The energy, the direction, and the current density of the ion beam can be adjusted intentionally because the sputtering species

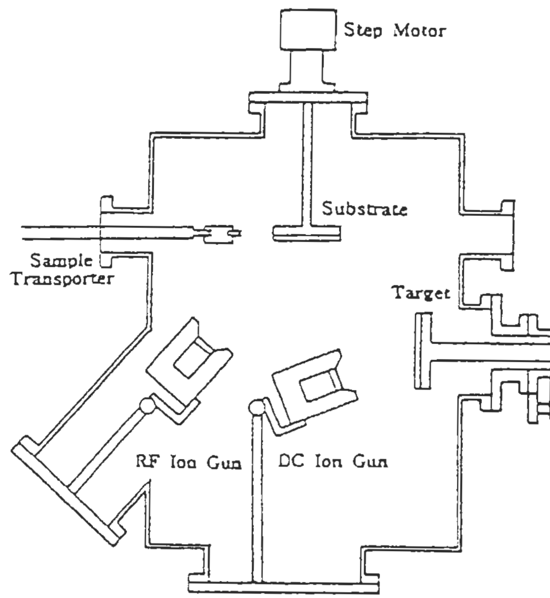

Fig.1 Schematic drawing of the dual ion sputter deposition (IBSD) system

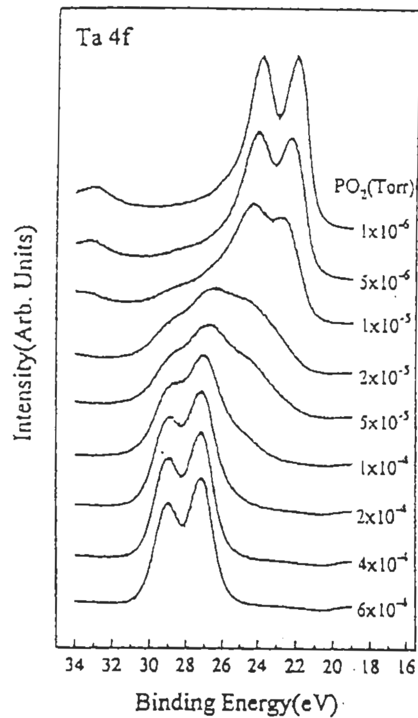

Fig.2 XPS spectra of Ta oxide thin film depending on the oxygen partial pressure

are produced out of the plasma. 2) The temperature of the substrate can be minimized because the plasma does not contact the substrate directly. 3) The deposition can be processed in the reactive gas to form a compound thin film. 4) The thin film modification can be achieved using extra energy source. 5) Several targets can be used at the same time to form a composite thin film. With this apparatus, oxide composite thin film and metal alloy thin film are prepared for the standard materials.

(a) Ta_2O_5/Ta multilayer thin film

In the Ta_2O_5/Ta multilayer thin film, the Ta_2O_5 layer has been deposited on Si(100) substrate by the reactive sputter deposition, that is, during the sputtering O_2 gas flow was introduced on the target. It has been found that the oxidation state of Tantalum oxide was determined by the partial pressure of oxygen. As shown in Fig. 2, Ta can be completely oxidized at the oxygen partial pressure of above 3 X 10^{-4} Torr. For Ta layer, the target was sputtered without the O_2 gas flow. The choice of deposition conditions and the impurities elimination can be made by *in-situ* analysis of the sample. The pure Ta target was purchased from the Pure Chemical Co., Japan. The substrate was rotated by 60 rpm for the homogeneity on the 3" silicon. The thickness was controlled with the deposition time. The deposition rate was determined by TEM measurement of a pre-deposited thin film. The multilayer thin film produced by this method shows uniform thickness and well-defined interface. Considering the effects of ion beam mixing and surface microstructure of the film, the thickness of each layer was determined to be about 30 nm and 6 nm for Ta_2O_5 and Ta, respectively. The pattern of the sample is $(Ta_2O_5/Ta)_3/Ta_2O_5/Si$ with the thickness of 34.2, 6.1, 32.4, 6.2, 31.9, 6.2, and 29.4 nm for each layer, which were measured using TEM. By SIMS using Ar^+ ion with the incidence angle of 60^0, the depth profile of this sample was obtained. The depth resolution of each Ta_2O_5/Ta interface is

measured to be 2.1, 2.1, 2.6 nm. (See Fig. 3)

(b) Ta_2O_5/SiO_2 multilayer sample

This sample has been designed for the depth profile of SIMS without matrix effect. Because of matrix effect, the sputtering yield of an element changes drastically. The data with matrix effect cannot tell us the exact performance of the instrument. The sample was deposited with the same method as described above; reactive sputter deposition from both Ta and Si targets. In order to get rid of the charging problem during the depth profile, the thickness of SiO_2 was made as thin as possible. It is found that with the thickness of 1 nm the depth resolution can be obtained. The sample pattern is $(Ta_2O_5/SiO_2)_6$/ Ta_2O_5/Si with the thickness of 18.8, 1.0, 18.6, 1.0, 18.6, 1.0, 18.4, 1.0, 18.6, 1.0, 19.0, 1.0, 18.0 for each layer. The interface of the sample was well developed and quite flat. In Fig. 4, the depth profile obtained by SIMS is presented. The depth resolution for the interface of Ta_2O_5/SiO_2 is about 2.1 nm and this value does not change with the depth.

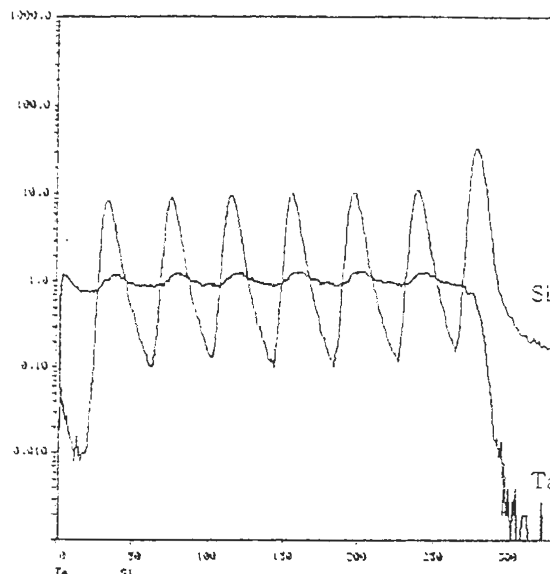

Fig.4 Depth profile of $(Ta_2O_5/Ta)_6/Ta_2O_5$/Si multilayer thin film by SIMS with 3keV Ar+ ion and the incidence angle of 60^0.

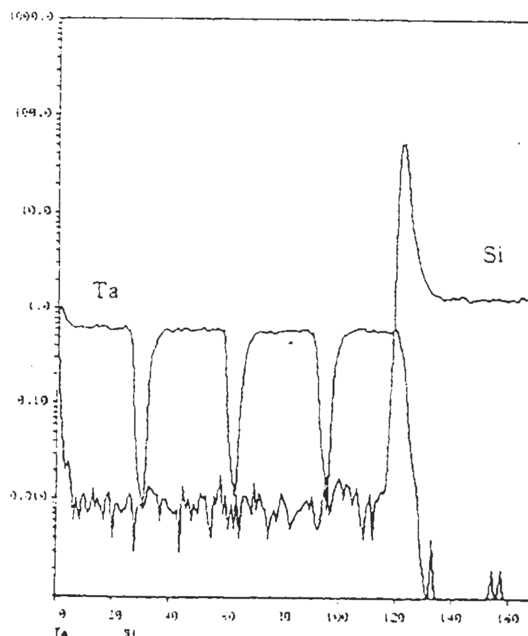

Fig.3 Depth profile of $(Ta_2O_5/Ta)_3/Ta_2O_5$/Si multilayer thin film by SIMS with 3keV Ar+ ion and the incidence angle of 60^0.

(2) Ion implanted samples for the quantitative surface analysis by SIMS

Metal ion implanted standard materials have been developed for the quantitative depth profiling analysis of metallic impurities by SIMS. The dose density of the implanted metal ions must be low enough to ignore the matrix effect. Metal ions produced from CHORDIS ion source with 15 keV energy were accelerated by 85 keV energy after mass separation to make the total energy of 100 keV implantation. For the uniformity, the ion beam was rastered by scanning system and the substrate holder was rotated with about 30 rpm. ^{52}Cr and ^{48}Ti ions were implanted into 3" silicon wafer with the ion dose in the range of 10^{14} ions/cm^2. The dose density was controlled by ion dosimetry and certified by RBS and SIMS. The dose density by SIMS analysis was calculated from the ion implanted standards purchased from Charles Evans & Associates. Taking several measurements of 10 mm X 10 mm pieces by RBS give the

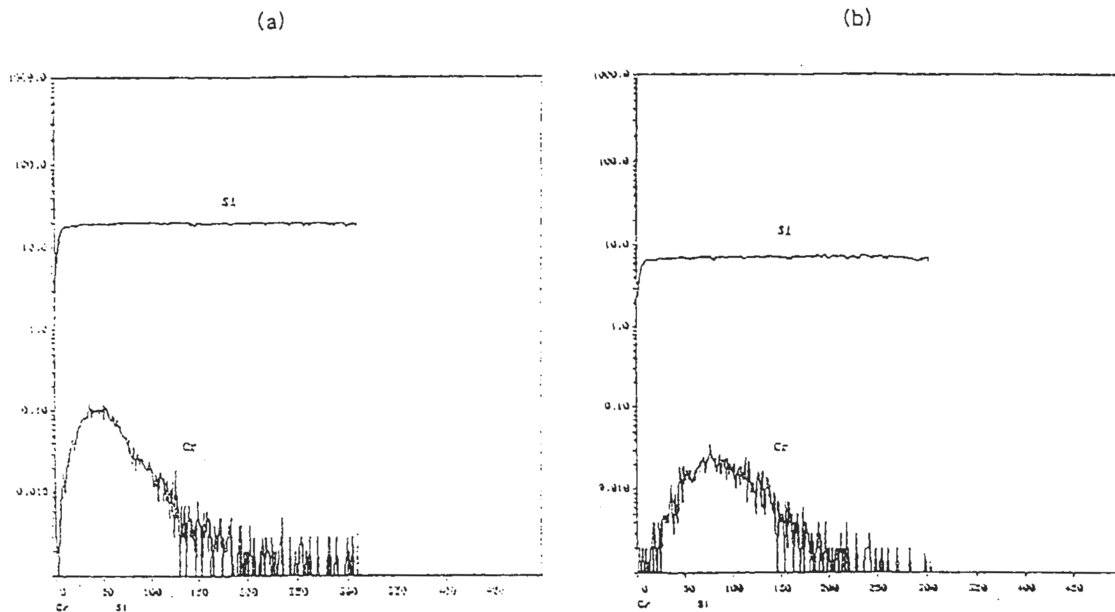

Fig. 5. SIMS depth profile of 100 keV Cr^{+} ion implanted CRM(a) and 200 keV Cr+ ion implanted sample from Charles Evans & Associates.

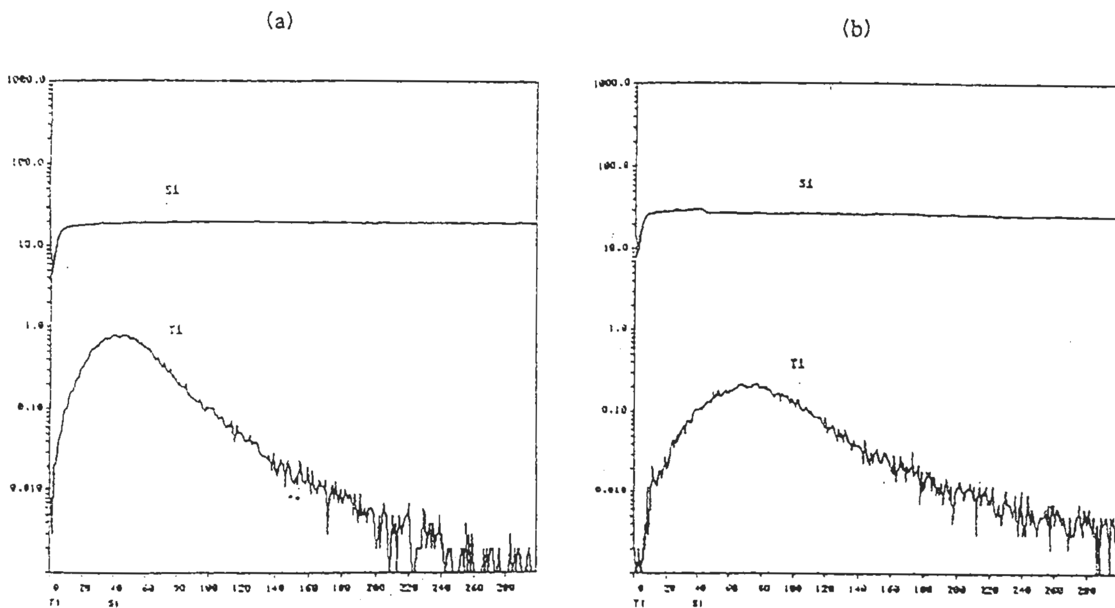

Fig. 6. SIMS depth profile of 100 keV Ti^{+} ion implanted CRM(a) and 200 keV Cr+ ion implanted sample from Charles Evans & Associates.

average dose density of 2.22×10^{14} ions/cm^2 for Cr and 3.5×10^{14} ions/cm^2 for Ti. These values are almost same as those obtained by SIMS); 2.8×10^{14} ions/cm^2 for Cr and 3.6×10^{14} ions/cm^2 for Ti. (See Fig. 5 for Cr and Fig. 6 for Ti)

(3) Multilayer sample for the quantitative surface analysis by XPS and AES

Mainly, XPS and AES have been applied to quantify the composition of the surface. However, there is no technique for the

absolute quantitative surface analysis yet. In order to accomplish the quantitative surface analysis, the standard material with the known composition exactly should be needed. Two kinds of the alloy Co-Ni and Au-Cu have been developed as standard materials and studied by many researchers. These sample does not show any surface segregation or preferential sputtering phenomena, which change the concentration on the surface. In practice, such phenomena have occurred very frequently. The Pt-Co alloy was chosen because it would show the preferential sputtering during ion beam bombardment due to the mass difference between the constituents.

(a) Pt-Co alloy multilayer thin film

The three kinds of the alloy were designed; Pt75Co25, Pt50Co50, and Pt25Co75. Generally, the standard materials for the quantitative surface analysis take the foil form. During the preparation of such a form, the non-homogeneity and the surface roughness can occur on the surface. And only the information on the chemical composition can be obtained from this kind of sample. The proposed alloy samples are prepared in the form of thin film on Si(100) not only for the compositional analysis but also for the sputtering yielding measurement and the depth resolution analysis. And by IBSD, the homogeneity and the roughness on the sample can be controlled very well.

By putting Pt and Co targets adjacent to each other and controlling the position to the sputtering beam, the alloy thin films have been deposited. Depending on the ratio of sputtering beam area, different compositional alloy can be obtained. Using *in-situ* analysis by XPS and then adjusting the target holder position, the deposition condition should be settled till the desired concentration has been reached. The target materials with the purity of 99.99% was purchased from Atomeric Chemicals, U.S.A. During deposition, the composition and impurity control have been made by in-situ SIMS and XPS analysis. After deposition, RBS measurements were performed to confirm the final compositional information.(See Fig. 7)

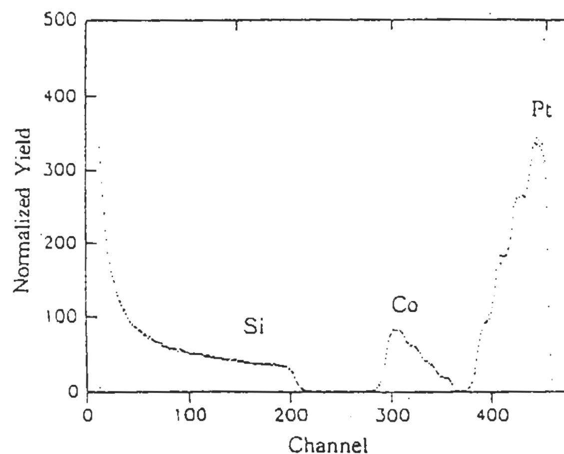

Fig. 7. RBS spectrum of the proposed standard material of Pt-Co alloy multilayer thin film.

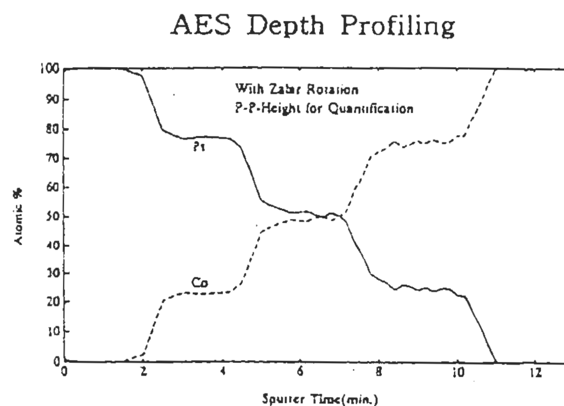

Fig. 8. AES spectrum of the proposed standard material of Pt-Co alloy multilayer thin film.

The thickness of each layer in the sample is as following; 22.5 nm for Pt100, 22.5 nm for Pt75Co25, 23.8 nm for Pt50Co50, 25.0 nm for Pt25Co75, and 25.0 nm for Co100.

AES depth profile has been conducted for this sample, as shown in Fig. 8.

3. Summary

In KRISS, several standard materials have been developed for depth profile and quantitative surface analysis using IBSD and ion implantation methods. For depth profile , two kinds of multilayer thin films are proposed and characterized; $(Ta_2O_5/Ta)_3/Ta_2O_5/Si$ and $(Ta_2O_5/SiO_2)_6/Ta_2O_5/Si$. For quantitative surface analysis, specially for microanalysis by SIMS, ion implanted samples are produced and the multilayer thin film of Pt-Co alloy is introduced and characterized.