Quantitative Depth Profiling of Argon in Tungsten Films by Secondary Ion Mass Spectrometry

Hideyuki YAMAZAKI

Toshiba Corporation, Research and Development Center, 8 Shinsugita-cho, Isogo, Yokohama 235-8522, Japan

Depth profiling of Ar in Ar-implanted tungsten (W) films with an excellent detection limit was investigated by secondary ion mass spectrometry (SIMS). Depth profiles of Ar with the detection of Ar^+ and ArCs^+ secondary ions, which were produced by O_2^+ and Cs^+ primary ions, respectively, were compared in view of the detection limit and the depth resolution. The detection limit of Ar monitoring Ar^+ was limited by the carbon- and oxygen-containing molecular ion (C_2O^+) in the sample as well as in the SIMS instrument. It was observed that some of the Ar^+ ions were produced in the vacuum above the sample surfaces, whereas the ionization of almost all C_2O^+ occurred at the samples. By using different energy spectra between Ar^+ and C_2O^+ , we showed that the energy-filtering technique is advantageous for suppressing C_2O^+ ion detection. It is also confirmed that the ArCs^+ secondary ion is only slightly by the C_2OCs^+ mass-interference ion. A detection limit of $4 \times 10^{18} \text{ cm}^{-3}$ for monitoring Ar^+ and $3 \times 10^{16} \text{ cm}^{-3}$ for monitoring ArCs^+ was achieved under a primary-ion current density of 0.16 mA/cm^2 . The detection of ArCs^+ ion rather than Ar^+ was found to be superior in the detection limit and the depth resolution. We conclude that SIMS is useful for the determination of the Ar depth distribution in W films.

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Introduction

Rare gases are universally used as working gases of DC, RF, magnetron and ion beam sputtering sources. Therefore, rare gas species are incorporated unintentionally in films during growth by sputter deposition. The increase in the amount of trapped rare gas species leads to a change in the structure and electrical properties of the film. For example, the compressive stress in sputter-deposited TiC^1 and Mo^2 films is related to the trapped argon concentration in the films. The resistivities of silver and tungsten films increase in proportion to the incorporated argon concentration.³

Secondary ion mass spectrometry (SIMS) has been widely used to characterize trace elements in thin films and solid surfaces due to its high detection power and large dynamic range for surface-distribution analysis.⁴⁻⁷ However, the ionization probability of secondary ions mainly depends on three factors:⁸⁻¹² (i) the atom's ionization potential (IP) for measuring positive secondary ions, (ii) the atom's electron affinity (EA) for measuring negative secondary ions and (iii) the surface work function. Thus, it is difficult to achieve lower detection limits of the rare gas species because of their high IP (12.13 – 24.59 eV) and low EA (0 eV).¹³ The earliest report on depth profiles for He implanted in Si and GaAs was by Wilson, Deline and Hopkins,¹⁴ who demonstrated that He densities greater than about 10^{18} cm^{-3} could be measured by an oxygen primary ion beam. It was noted that detecting MCs^+ (M is the element to be analyzed) secondary ions formed under the bombardment of Cs^+ primary ions can be applied to a SIMS analysis of the rare gases. Ray and co-workers¹⁵ have shown the detection limits for Ar and Kr in Si, Ge and GaAs using Cs^+ (or O_2^+) primary ions and monitoring ArCs^+ (or Ar^+) secondary ions. Gnaser and Oechsner¹⁶ investigated the He depth profile

in Si by SIMS and monitored HeCs^+ secondary ions. The detection limits of He, Ar and Kr measured by various authors are summarized in Table 1. As mentioned above, the properties of sputter-deposited films are related to the amount of Ar present in the films. Therefore, it is important to determine the depth profile of Ar with a lower detection limit. To the author's knowledge, there are no experimental data on the SIMS detection limit of Ar in tungsten (W).

In this paper, we report on the depth profiling of Ar in W films with monitoring Ar^+ and ArCs^+ secondary ions. First, the influence of secondary ion's kinetic energy filtering on the detection limit of Ar was evaluated in order to resolve the mass-interference ion. We also investigated the detection limits of Ar in W as a function of the primary-ion current density. Next, the depth resolutions of Ar profiles monitoring Ar^+ and ArCs^+ were compared.

Experimental

The samples used were ^{40}Ar implanted and non-implanted tungsten (W) films deposited on silicon wafers by a sputtering technique. In order to remove native oxide and organic contaminants, silicon wafers were chemically cleaned prior to the deposition of W films. W films (450 nm thick) were deposited by ion-beam sputtering with Xe sputtering gas at room temperature. The implant energy and dose of ^{40}Ar were 100 keV and $5 \times 10^{15} \text{ cm}^{-2}$, respectively.

All SIMS experiments were performed on a Cameca IMS-4f instrument using either O_2^+ or Cs^+ primary ions. The O_2^+ and Cs^+ primary ion beams were accelerated to 10 kV. The sample holder was biased to normal +4.5 kV in order to eject positive secondary ions. Therefore, the primary ion beams reach the sample surface with an impact energy of 5.5 keV. The sample

Table 1 SIMS detection limits of rare gases

Matrix	Primary ion	Primary-ion current density (mA/cm ²)	Detection limit (atoms/cm ³)			Ref.
			He	Ar	Kr	
Si	O ₂ ⁺ —	—	~10 ¹⁸	—	—	Wilson <i>et al.</i> [14]
Si	O ₂ ⁺ (5.5 keV)	35–40	—	3 × 10 ¹⁸	—	Ray <i>et al.</i> [15]
Si	O ₂ ⁺ (6.0 keV)	—	—	6 × 10 ¹⁹	—	Stevie <i>et al.</i> [17]
Ge	O ₂ ⁺ (5.5 keV)	35–40	—	7 × 10 ¹⁸	2 × 10 ¹⁸	Ray <i>et al.</i> [15]
GaAs	O ₂ ⁺ —	—	~10 ¹⁸	—	—	Wilson <i>et al.</i> [14]
GaAs	O ₂ ⁺ (5.5 keV)	35–40	—	2 × 10 ¹⁸	~10 ¹⁹	Ray <i>et al.</i> [15]
Si	Cs ⁺ (8.0 keV)	6	—	2 × 10 ¹⁸	6 × 10 ¹⁸	Ray <i>et al.</i> [15]
Si	Cs ⁺ (5.5 keV)	0.06–0.32	~10 ¹⁹	—	—	Gnaser, Oechsner [16]
Ge	Cs ⁺ (8.0 keV)	6	—	4 × 10 ¹⁷	~10 ¹⁹	Ray <i>et al.</i> [15]
GaAs	Cs ⁺ (8.0 keV)	6	—	7 × 10 ¹⁷	~10 ¹⁹	Ray <i>et al.</i> [15]

potential can be varied between +4375 V and +4625 V for recording energy distributions of positive secondary ions or detecting positive secondary ions with the energy filtering technique. The primary-ion current was varied between 200 nA and 500 nA and the raster size between (75 μm)² and (250 μm)², namely, primary-ion current densities (ion current/raster area) ranging from 0.16 to 3.5 mA/cm². The value of the primary-ion current was monitored in the standard IMS-4f Faraday cup. Positive secondary ions of M⁺ and MCs⁺ produced by O₂⁺ and Cs⁺ primary beams, respectively, were detected by an electron multiplier. The secondary ions were collected from the central region of the sputtered craters in order to minimize the crater edge and sidewall effects. For all depth-profiling measurements, the energy window of the kinetic energy filter of secondary ions was symmetrically opened to 55 eV (total energy band pass of 110 eV). The energy window can be moved by ± 55 eV. The crater depth was measured with a Dektak 3030 profilometer. The conversion of ion counts (count/s) to concentration (atoms/cm³) was accomplished using the relative sensitivity factors (RSFs).⁵ The detection limits were defined as the average background signal at the constant level measured in the tail of the implantation profile. The kinetic energy spectra of the secondary ions were determined by varying a sputtered ion accelerating potential of around +4.5 kV by computer control.

All measurements were performed after 15 h pumping after sample introduction into the sample chamber. The vacuum in the sample chamber during the measurement was 1.3–2.7 $\times 10^{-7}$ Pa (1–2 $\times 10^{-9}$ Torr).

Results and Discussion

Energy filtering

As a result of a SIMS analysis, it was confirmed that the W films contain such light elements as H, C and O. These light elements also exist in the SIMS sample chamber as residual gases. No other impurities were observed. Therefore, the detection of ⁴⁰Ar and ⁴⁰Ar¹³³Cs⁺ is influenced by the ¹²C₂¹⁶O⁺ and ¹²C₂¹⁶O¹³³Cs⁺ mass interference molecular ions, respectively. There are two techniques used to resolve the mass interfaces: high mass resolution and energy-filtering techniques.^{5,7} However, a high-mass resolution technique is undesirable for routine measurements because adjusting the instrument is troublesome due to hysteresis effects. The analysis of Ar in W would require a mass resolution ($m/\Delta m$) of ≈ 1230 for Ar⁺/C₂O⁺ and ≈ 5320 for ArCs⁺/C₂OCs⁺. This mass resolving power

Fig. 1 Secondary-ion energy spectra for ¹²C₂O⁺, ⁴⁰Ar⁺ using an O₂⁺ primary ion and ⁴⁰Ar¹³³Cs⁺ using a Cs⁺ primary ion. The ¹²C₂O⁺ ions were obtained from non-implanted W samples. The ⁴⁰Ar⁺ and ⁴⁰Ar¹³³Cs⁺ ions were obtained from ⁴⁰Ar implanted W samples.

exceeds the capability of typical quadrupole instruments where $m/\Delta m \leq 500$.⁵ On the other hand, energy filtering is available when the ion kinetic-energy spectra between analyte and interface ions are different.

The sputtered species having high ionization potentials, such as rare gases, are ionized almost entirely by gas-phase ionization processes which occur in a vacuum above the sample surfaces.¹⁸ In contrast, the ionization of sputtered C and O containing contaminants would have taken place at the sample surfaces. Therefore, the C and O containing molecular ions must be suppressed by an energy-filtering technique. In order to verify the difference in the ionization mechanism between Ar⁺ and C₂O⁺ sputtered from the W, the energy spectra of these ions were examined. The results obtained with 5.5 keV O₂⁺ primary ions are shown in Fig. 1. The energy spectrum of the ArCs⁺ ion under 5.5 keV Cs⁺ bombardment is also shown in Fig. 1. In contrast to C₂O⁺ and ArCs⁺, Ar⁺ ions are primarily observed on the negative-energy side in the spectrum ("prepeak ions"). The prepeak ions are ascribed to post-ionization of sputtered neutrals in the strong electric field in front of the sample. Thus, it is indicated from Fig. 1 that some of Ar⁺ is formed by the gas-phase ionization processes, as already mentioned in Ref. 18, whereas the ionization of C₂O occurs at the sample surfaces. It can be expected that suppression of C₂O⁺ is achieved when the energy spectra are shifted by offsetting the sample voltage so as to accept only ions where

Fig. 2 Detection limits of Ar in W measured with various sample voltages, monitoring Ar^+ (●) and ArCs^+ (□) obtained with O_2^+ and Cs^+ primary ion beams, respectively. The current density of both primary ions was 0.16 mA/cm^2 .

energies lie on the low-energy side. In order to achieve the lowest detection limit of Ar, the optimum condition of energy filtering was investigated as a function of the sample voltage. The results are shown in Fig. 2. It can be seen that in comparison with the normal analytical condition, the detection limit of Ar monitoring Ar^+ is improved by a factor of 4 when the sample voltage is increased from normal +4500 V to +4530 V under a slit width of 110 eV in the kinetic energy filter. It was found that the energy-filtering technique for an O_2^+ bombardment analysis is useful in avoiding interference from C_2O^+ ions. No further improvement of the detection limit was observed when the energy spectra were shifted by more than 30 eV due to a loss of the signal intensity of Ar^+ . Energy filtering had no effect on improving the detection limit of Ar monitoring ArCs^+ , because, as shown in Fig. 3, the influence of C_2OCs^+ interference ion can be negligible due to the lower background signal of C_2OCs^+ . Returning Fig. 2, it can be seen that the Ar detection limit using ArCs^+ is approximately 2 orders of magnitude lower than that determined for Ar^+ . The reason is that, in addition to no problem of C_2OCs^+ mass interference ion, the yield of ArCs^+ is much more sensitive than that of Ar^+ , as shown in Fig. 1.

Figure 4 summarizes the Ar detection limits monitoring Ar^+ and ArCs^+ , as a function of the O_2^+ or Cs^+ primary-ion current density (J_{O_2} or J_{Cs}). It is clear that there is a linear dependence of the Ar detection limit on the primary-ion current density. The correlation between the detection limit (c) and the primary-ion current density (J_{O_2} or J_{Cs}) can be expressed as follows: $c(\text{Ar}^+) \propto 6 \times 10^{17}/J_{\text{O}_2}^{1.3}$, $c(\text{ArCs}^+) \propto 4 \times 10^{15}/J_{\text{Cs}}^{1.1}$. Increasing the primary current density by more than $J_{\text{O}_2} = 1.0 \text{ mA/cm}^2$ or $J_{\text{Cs}} = 3.0 \text{ mA/cm}^2$ did not result in the expected detection limit. The reason for this phenomenon would be the crater edge and sidewall effects due to a poorly focused primary beam and a small-area analysis.^{5,7,19}

Depth resolution

Figure 5 shows examples of the Ar depth profiles in W, obtained by monitoring Ar^+ with O_2^+ primary-ion ($J_{\text{O}_2} = 0.32 \text{ mA/cm}^2$) and monitoring ArCs^+ with Cs^+ primary-ion ($J_{\text{Cs}} = 0.32 \text{ mA/cm}^2$). The erosion rates of O_2^+ and Cs^+ primary-ion

Fig. 3 SIMS depth profiles of C_2O^+ and C_2OCs^+ , obtained with O_2^+ and Cs^+ primary ion, from non-implanted W samples. The primary-ion current density was 0.16 mA/cm^2 .

Fig. 4 Detection limits of Ar in W, as a function of O_2^+ or Cs^+ primary-ion current density. The detected secondary ions were Ar^+ (●) and ArCs^+ (□) obtained with O_2^+ and Cs^+ primary ion beam, respectively. An offset voltage of 30 V (sample voltage: +4530 V) was applied for detecting Ar^+ .

beam measurements were 0.4 nm/s and 1.5 nm/s , respectively. On the basis of the optimum condition discussed in the previous section, energy shifting of 30 eV was applied in the detection of Ar^+ . As shown in Fig. 5, the depth resolution of the Ar^+ profile is worse in comparison with the ArCs^+ profile. It has been documented that the ion bombardment of solid surfaces produces a surface topography^{5,20-22} which leads to a degradation of the depth resolution.⁵ The surface topography of polycrystals is more pronounced than that of single crystals according to the experimental results obtained from the O_2^+ bombardment of Cu.²² Therefore, the result of Fig. 5 is attributed to the difference in the surface topography between O_2^+ and Cs^+ sputtering; the development of the W surface topography would be more pronounced for O_2^+ than for Cs^+ bombardment. It is also noted that in contrast to ArCs^+ , the poor detection limits of Ar monitoring Ar^+ result from the inferior depth resolution of the Ar^+ profile.

Fig. 5 SIMS depth profiles of 100 keV Ar implanted in W. Detected secondary-ions were Ar^+ and ArCs^+ obtained with O_2^+ and Cs^+ primary-ion beam, respectively. The current density of both O_2^+ and Cs^+ primary-ion was 0.32 mA/cm^2 . An offset voltage of 30 V (sample voltage: +4530 V) was applied for detection of Ar^+ .

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