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Characterization of sputtered W–Si–N thin films by a monoenergetic positron beam

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Abstract

A monoenergetic positron beam was employed to characterize the uniformity and the microstructural variation of thermally treated W–Si–N thin film. As the annealing temperature is increased, positrons are found to be progressively trapped in sites rich in silicon. This behavior is explained by the formation of W clusters from which positrons are favorably trapped into the Si–N amorphous matrix. Positron results are discussed together with information obtained on similar samples by Rutheford backscattering, infrared spectroscopy and transmission electron microscopy measurements.

Keywords: Ternary alloys; W–Si–N; Positron annihilation spectroscopies; Doppler broadening; Coincidence doppler broadening; Monoenergetic positrons

1. Introduction

The recent introduction of Cu as conductive material in microelectronic devices has required the development of a diffusion barrier to be inserted between Cu and the Si or Si based dielectrics to avoid the formation of Cu-silicides (Ramberg et al., 2000).

Ternary systems of the types TM–Si–N, consisting of alloys of transition metal (TM = Ti, Ta, W), silicon and nitrogen, are candidates for such diffusion barriers (Nicolet and Gianque, 2001; Vomiero et al., 2004a,b). A good barrier must not interact with Si and Cu but also be electronically conductive and it should have an amorphous microstructure because grain boundary is a typically rapid diffusion path for chemical species.

In this work, we report an experimental characterization of W–Si–N alloy thin films grown on monocrystalline silicon substrate. The films were deposited with different N content and thermally treated at different annealing temperatures. Positron Doppler-broadening spectroscopy (DBS) and Doppler-broadening in coincidence spectroscopy (C-DBS) have been carried out with a slow positron beam. Positron results are presented and discussed together with results obtained by fast Fourier infrared spectroscopy (FTIR), transmission electron microscopy (TEM) and Rutheford backscattering spectroscopy (RBS) on similar samples (Vomiero et al., 2004a,b).

2. Experimental

The W–Si–N thin films were deposited on monocrystalline Si substrate using a 2″ source in RF mode

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(13.56 MHz) from W_5Si_3 target, via reactive magnetron sputtering in Ar/N_2 gas mixtures. The composition of Ar/N_2 reactive gas was controlled, in order to obtain films with the desired N content. During the sputtering the total pressure was maintained at 0.4 Pa. Isothermal treatments were performed in vacuum for 1.5 h at 600–750–900–980 °C.

The stoichiometric composition of the deposited films was checked by RBS using a 2.2 MeV $4He^+$ beam while the density was estimated by combining thickness and RBS measurements (Vomiero et al., 2004b).

In this work, we have studied two film series with the following composition $W_{37}Si_{17}N_{46}$ and $W_{40}Si_{18}N_{42}$ as measured by RBS. The film with composition $W_{37}Si_{17}N_{46}$ shows a thickness of 186 nm and a density of 7.9 g/cm^3 while the film with composition $W_{40}Si_{18}N_{42}$ has a thickness of 158 nm and a density of 8.5 g/cm^3. With this nitrogen content, in the as-grown films, FTIR measurements point out that both Si and W bonds with nitrogen are present; moreover, in a wide range of N content (N_{21}–N_{49}) the as-grown films were found to be amorphous (Vomiero et al., 2004b). The positron DBS and C-DBS measurements were carried out with a monoenergetic positron beam (Zecca et al., 1998) equipped with two Camberra low-noise high-purity germanium (HpGe) detectors in a 180° configuration at 3.5 cm from the samples. The two HpGe detectors had 45% efficiency and 1.4 keV energy resolution at 511 keV.The 511 keV annihilation line was characterized with the S parameter calculated as the ratio of the counts in the central area of the peak ($|$ 511- E_γ $|$ $\leqslant$ 0.85 keV) to the total area of the peak ($|$ 511- E_γ $|$ $\leqslant$ 4.25 keV), with E_γ the Doppler shift in energy of the annihilation γ-ray. For the DBS measurements, about 2×10^4 counts were acquired in the 511 keV line for each positron implantation energy E. This corresponds to a statistical error of 1×10^{-3} on the S parameter. For the C-DBS measurements about 2×10^7 counts were acquired in the annihilation line.

3. Results and discussion

The S_n ($S_n = S_{measured}/S_{bulk\text{-}Si}$) vs. E curves (Fig. 1), obtained by DBS measurements, were fitted by the VEPFIT program (van Veen et al., 1990). The fits point out the presence of two different layers in the films. The first one has an average thickness of 10±2 and 8±3 nm for the samples of the $W_{37}Si_{17}N_{46}$ and of the $W_{40}Si_{18}N_{42}$ series, respectively. The thickness of this layer does not change with the thermal treatment except in the sample $W_{40}Si_{18}N_{42}$ annealed at 980 °C. In both the series, the S_n values of the first layer result lower than in the second one. Moreover the S_n values of both layers increase with the increase of the annealing temperature (see Table 1). In order to have more information on the microstructural characteristics of the two layers, the C-DBS curves were measured for the samples $W_{40}Si_{18}N_{42}$ at 0.2 keV (0.4 nm, first layer) and 2 keV (15 nm, second layer) positron implantation energy. Ratio curves between the measured curves and the Si reference curve were constructed. In Fig. 2 only ratio curves of the samples annealed at 750 and 980 °C are shown for clarity. A W ratio curve to Si is also presented for the discussion of the data.

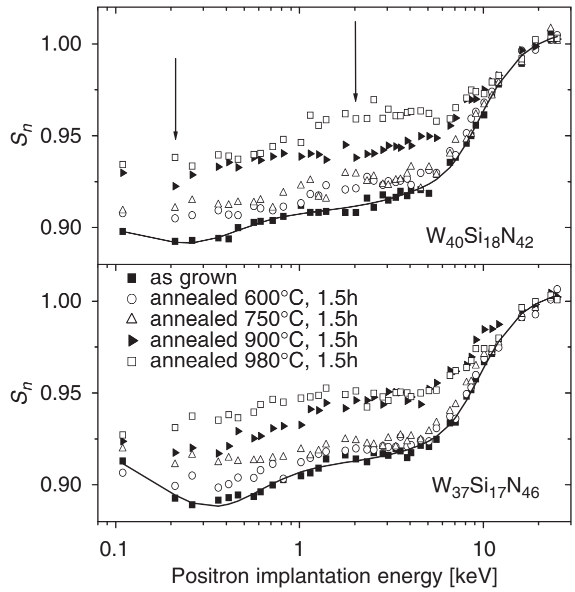

Fig. 1. S_n vs. positron implantation energy for $W_{40}Si_{18}N_{42}$ and $W_{37}Si_{17}N_{46}$ films as-grown and thermal treated. The arrows mark the energies where C-DBS curves were measured. As an example the best fits for the as deposited samples of both series are reported.

The ratios indicate that at 0.2 keV the positrons annihilate in sites slightly richer in W and poorer in Si in the first layer with respect to the second one (Fig. 2). Moreover, the positron annihilation signal from W decreases with the thermal treatments, in both the layers.

This chemical change pointed out by the annihilation characteristics, after annealing, is in agreement with the change observed by RBS, FTIR and TEM, on samples with similar composition (Vomiero et al., 2004a,b). However, it is important to emphasize that these techniques cannot distinguish the presence of different layers but they give only average information on the film's characteristics.

RBS measurements point out that the main result of the annealing is the loss of N at temperatures higher than 600 °C. Instead, no W or Si loss was found. FTIR spectroscopy analysis indicates the formation of Si–N bonds (melting point ~1900 °C, David R. Lide (1998–1999)) in the as-grown samples. These measurements suggested the presence of a structure similar to

Table 1
Sn values, positron diffusion length (L_+) and layers thickness of the samples of the two series

Samples	Treatment	Layer I			Layer II		
		Thickness (nm)	S_n ±0.001	L_+ (nm)	Thickness (nm)	S_n ±0.001	L_+ (nm)
$W_{37}Si_{17}N_{46}$	As grown	9±2	0.906	1.1±0.1	177	0.915	106±8
	600°C	9±2	0.914	2.3±0.2	177	0.915	106±7
	750°C	10±2	0.919	2.0±0.2	176	0.922	100±8
	900°C	12±2	0.939	3.7±0.3	174	0.941	101±14
	980°C	10±2	0.933	10±1	176	0.943	73±7
$W_{40}Si_{18}N_{42}$	As grown	9±4	0.903	1.7±0.2	149	0.921	66±13
	600°C	10±4	0.917	2.8±0.6	148	0.918	94±11
	750°C	9±4	0.921	4.0±0.3	149	0.923	66±7
	900°C	9±4	0.935	1.3±0.2	149	0.945	90±20
	980°C	5±4	0.935	0.9±0.8	153	0.959	1

The L_+ in the Si substrate was found to be 200 nm.
Data obtained by VEPFIT program

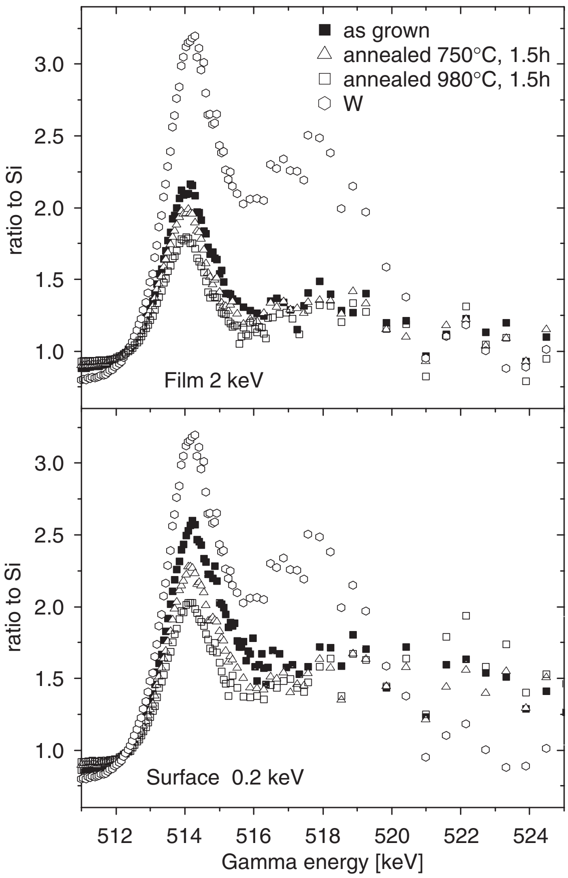

Fig. 2. Coincidence ratio curves referred to Si. The curves were measured in the samples of the series $W_{40}Si_{18}N_{42}$ at 0.2 and 2 keV corresponding to a depth of 0.4 and 15 nm, respectively. The W ratio curve to Si is also shown.

that of an amorphous Si_3N_4 network. Since the intensity of the Si–N band does not decrease after the thermal treatments, it is possible to deduce that the released N is not due to nitrogen directly bound to Si but it comes out from weaker W–N bonds (melting point ~600 °C, David R. Lide (1998–1999)). Moreover, FTIR spectroscopy reveals that the annealing induces the segregation of a more ordered phase within the amorphous matrix of Si_3N_4. TEM measurements show that the as-grown ternary films are characterized by an amorphous structure. After annealing at high temperature (900 °C), the film with low N concentration ($W_{58}Si_{21}N_{21}$) shows the precipitation of W grains in BCC phase, as indicated by selected area electron diffraction (SAED) patterns (Vomiero et al., 2004b). TEM plan view images suggest the presence of a high density of grains uniformly distributed over film surface; grains average diameter varies between 4 and 10 nm, even if wider grains with diameter up to 20 or 30 nm are also present. TEM analysis on cross-sections confirms the presence of a high density of W grains uniformly distributed over film thickness, thus indicating the absence of a preferred region for crystallization process (Felisari, 2005). No precipitation of W grains was observed by TEM in the sample with higher N concentration ($W_{35}Si_{16}N_{49}$). Tungsten preserves its amorphous phase nevertheless the loss of N.

The possible re-arrangement of very small W amorphous clusters, not detected by TEM, and embedded in the Si–N matrix, can explain the increase of Si signal and the decrease of W signal. With the loss of N and the formation of the W clusters, positrons are favorably trapped in the Si–N amorphous matrix. The increase of the fraction of positrons annihilating in Si–N matrix also explain the S_n increase during annealing. Indeed the S_n tungsten bulk value is very low (0.86).

According to this picture, the positron analysis points out the formation of small W clusters, not detected in TEM images, also in samples with high N concentration ($W_{40}Si_{18}N_{42}$–$W_{37}Si_{17}N_{46}$). Moreover, the wider change in the tungsten characteristic peaks in Fig. 2 at 0.2 keV with respect to 2 keV can be interpreted as a more intense segregation of W (larger loss of N) on the surface of the film than in the bulk of the film.

Positron diffusion length (Table 1) is higher in the samples with less W. L_+ strongly decreases in the samples annealed at 980 °C. This decrease can be probably associated to an increase of defect density due to the higher nitrogen release.

4. Conclusions

W–Si–N ternary films of two different compositions ($W_{40}Si_{18}N_{42}$ and $W_{37}Si_{17}N_{46}$) were characterized by DBS and C-DBS, before and after annealing in vacuum up to 980 °C. The measurements indicate the presence of a surface layer of about 10 nm in both series, richer in W and poorer in Si with respect to the bulk of the film. After thermal treatments an increase of positron annihilations in sites rich of Si (Si–N amorphouse matrix) was observed in both layers. This is explained by the formation of small amorphous W clusters induced by N release from W–N bonds. This segregation results more intense on the surface than in the film.

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