Barrier property of TiSiN films formed by low frequency, high density inductively coupled plasma process

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Abstract

A ternary barrier film TiSiN was prepared by low frequency, high density inductively coupled plasma (ICP) implantation of N into TiSi substrate. This leads to the formation of Ti–N and Si–N compounds in the ternary film. Using this technique, 5–20-nm-thick TiSiN films were successfully grown over different deposition conditions including external bias, argon gas flow rate and nitrogen plasma treatment time. Barrier film structure was characterized by X-ray diffraction (XRD). For compositional analysis, X-ray photoelectron spectroscopy was used. The diffusion study was carried out by depth profiling of Cu using time-of-flight secondary ion mass spectrometer (ToF-SIMS) after annealing treatment at various temperatures. Discussion on the relationship between the barrier performance and the film structures is made in an attempt to elucidate the controlling factor for Cu diffusion in such a mixed microstructure. The implication to process conditions is also discussed.

Keywords

Diffusion; TiSiN barrier; Cu metallization; Plasma implantation

1. Introduction

It is well known that copper is a fast diffuser in SiO_2 and Si [1]. Furthermore, copper creates silicon recombination centers [2], thus reducing the minority carrier lifetime and affecting the performance of silicon based devices. Therefore, an appropriate barrier layer material to prevent copper diffusion is required. According to International Technology Roadmap for Semiconductors 2003, beyond 100-nm device node, diffusion barrier thickness for copper was anticipated to be less than 10 nm [3]. Consequently, new material sets are being investigated to provide chemically, electrically and thermally stable diffusion barrier at such a thickness.

Many barrier materials have been investigated; these include Ta, TaN, TiSiN and TaSiN. The selection of the ternary metal–silicon–nitrides is based on their reduced diffusion pathway density and increased diffusion activation energy due to their amorphous microstructure and high inter-atomic binding energies [4,5].

In this paper, we report the study on the diffusion of Cu in a ternary TiSiN film. The film was produced by low frequency, high density inductively coupled plasma process (ICP). Effect of processing parameters on the layer thickness, sheet resistance and phase composition was reported elsewhere [6]. The focus of current work is to investigate the effect of plasma processing parameters, such as external bias, nitrogen plasma treatment time and argon gas flow ranging, on the diffusion of Cu in the TiSiN layer.

2. Experiment

The 50-nm TiSi (the actual stoichiometric composition should be Ti_xSi_y) film was fabricated by depositing a layer of Ti on silicon wafers first, followed by rapid thermal annealing at 750 °C (RTA1) and 850 °C (RTA2). High density nitrogen implantation into TiSi film was conducted in a low frequency, high density inductively coupled plasma reactor. The chamber was evacuated to $1x10^{-4}$Torr (base pressure) before the processing gases were introduced. Low frequency ~0.5 MHz has been applied for the inductive plasma production. Argon, hydrogen and nitrogen gases were used in our process. External bias of 100, 200 and 300 V were applied to the substrate to accelerate the implantation of nitrogen into the TiSi film. The nitrogen plasma treatment time was chosen to be 30 and 60 min and the argon gas flow rate varied from 10 to 30 sccm. Details of the processing parameters are shown in Table 1. The total gas pressure was maintained at $2x10^{-2}$Torr, the substrate temperature was between 200 and 300 °C, and the plasma power was 2 kW.

The thickness of the formed TiSiN (likewise the exact stoichiometric composition should be $Ti_xSi_yN_z$) ranges from 5 to 20 nm, depending on the process parameters [6]. To evaluate the performance of ICP TiSiN as a copper diffusion barrier, 50-nm-thick Cu film was sputter deposited onto the TiSiN layer. The resulting stacks were annealed in nitrogen ambient at 500 and 650 °C for 30 min. After annealing, copper was stripped off in a solution containing 260 g/l ammonium persulfate ($(NH_4)_2S_2O_8$) in H_2O. The depth profile of Cu, Ti, Si and N in the structures after annealing were characterized by time-of-flight secondary ion mass spectroscopy (ToF-SIMS) with 3 keVAr+ ion primary beam at a beam current of 50 nA.

3. Results and discussion

XPS analysis shows that there is a gradual change in the nitrogen atomic concentration through the thickness of TiSiN film as shown in Fig. 1. The atomic concentration of N ranges from 30% to 50%. Nitrogen is bonded with titanium and silicon, forming titanium nitrides and silicon nitrides, respectively, when N_{1s} peak are deconvoluted. This result is further confirmed in our XRD results as shown in Fig. 2.

Fig. 3 shows the ToF-SIMS depth profile of Cu/TiSiN/TiSi/Si structure without annealing. This is used as the reference for zero copper diffusion through the TiSiN film. It is found that there is a sharp decrease in copper concentration and the copper diffusion profile followed the implanted nitrogen profile. Fig. 4 shows the ToF-SIMS depth profile of Cu/TiSiN/TiSi/Si structure after 500 °C annealing. The effect of the external bias on the integrity of the barrier can be seen by comparing Fig. 4a, b and c, which show, respectively, the Cu, Ti, Si and N profiles in samples subjected to 100, 200 and 300 V external bias after annealing at 500 °C. In the samples subjected to 100 and 200 V external bias, the copper profile is similar to the one without annealing, which means that the penetration of copper through the TiSiN barrier is not significant. For thesample subjected to 300 V external bias, significant Cu diffusion is observed. When these samples are annealed at 650 °C, the same results are obtained, significant copper diffusion is observed only in the sample subjected to 300 V external bias. This implies that high external bias will degrade the barrier integrity.

Fig. 5 shows the ToF-SIMS depth profile of Cu/TiSiN/TiSi/Si structure after 500 °C annealing. The effect of the argon gas flow rate on the integrity of the barrier can be seen by comparing Fig. 5a, b and c. These samples were subjected to the same external bias (100 V) by comparing Fig. 5a, b and c. These samples were subjected to the same external bias (100 V)and nitrogen plasma treatment time (30 min). As shown in Fig. 5, no significant copper diffusion into TiSiN barrier film is detected. Similarly, as the annealing temperature increased to 650 °C, no significant copper diffusion can be observed except sample M, which has been subjected to 30 sccm argon gas flow and 30 min nitrogen plasma treatment. When the nitrogen plasma treatment time increased to 60 min at fixed external bias (100 V), significant copper diffusion is observed after annealing at 650 °C, regardless of argon gas flow rate as shown in Fig. 6a, b and c. It can be clearly seen that copper penetrates through the TiSiN barrier film. No significant copper diffusion can be observed for samples that annealed at 500 °C. It is shown from these results that the main factor that affects the barrier integrity is the external bias that applies to the substrate and the nitrogen plasma treatment time. Argon gas flow rate affects the TiSiN barrier performance at higher annealing temperature.

It is known that, below the Tammann temperature of about 50–67% of the absolute melting temperature of a polycrystalline solid, diffusion is not controlled by the bulk mechanisms, but rather by mechanisms associated with grain boundaries, pores, pinholes and dislocations [7]. For the samples that undergone an annealing process at a maximum temperature of 650 °C, which is about 29% and 43% of the TiN (3203 K) and Si_3N_4 (2173 K) melting temperatures, respectively, bulk diffusion should not control the transport of copper in the TiSiN layer. In our TiSiN samples, the plasma treatment causes crystallization of the barrier film. The TiSiN barrier film is heterogeneous mixtures as proved by the XRD results. The dominant phases are TiN and Si_3N_4 [6]. Thus, in the polycrystalline mixture of TiN and Si_3N_4 film, diffusion through grain boundaries and other defects become dominant.

Based on the above argument, the reason that 300 V external bias leads to easy diffusion by Cu could be due to the high speed bombardment of plasma ions towards the substrate at high external bias. This will give rise to higher density of defects in the formed film. As a result, barrier performance will be degraded. Ar treatment is used to dissociate the TiSi bond. Higher Ar flow rate promotes the formation of TiN and Si_3N_4, but at the same time, the lattice defects may also increase.

4. Conclusions

TiSiN barrier film produced by low frequency, high density inductively coupled plasma process containing two phases, TiN and Si_3N_4. The barrier properties are strongly influenced by the plasma process parameters. It is found that higher external bias and longer nitrogen plasma treatment time will lead to the degradation of the barrier performance. This is believed to be caused by higher density of defects due to the plasma treatment.

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Figure. 1 XPS depth profile of inductively coupled plasma TiSiN. Nitrogen ions are successfully introduced into Ti_xSi_y.

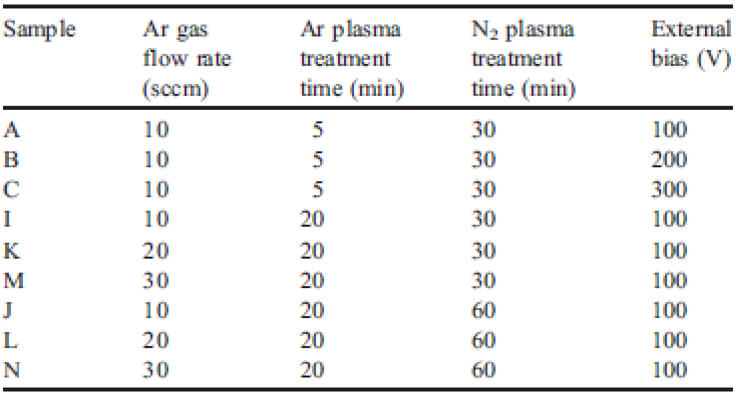
Figure. 2 XRD measurement of TiSiN film subjected to different argon gas flow rate, 60-min nitrogen plasma treatment time. Titanium nitrides and silicon nitrides are successfully formed.

Figure. 3 SIMS depth profile of Cu, Ti, Si, N for as-deposited sample without annealing

Figure. 4 SIMS depth profile of Cu, Ti, Si and N after annealing at 500 °C for samples subjected to external bias of (a) 100, (b) 200 and (c) 300 V.

Figure. 5 SIMS depth profile of Cu, Ti, Si and N after annealing at 500 °C for samples subjected to 100 V, 30-min nitrogen plasma treatment, but at different Ar gas flow rate. (a) 10, (b) 20 and (c) 30 sccm.

Figure. 6 SIMS depth profile of Cu, Ti, Si and N after annealing at 650 °C for samples subjected to 100 V, 60-min nitrogen plasma treatment, but at different Ar gas flow rate. (a) 10, (b) 20 and (c) 30 sccm.



Sample	Ar gas flow rate (sccm)	Ar plasma treatment time (min)	N_2 plasma treatment time (min)	External bias (V)
A	10	5	30	100
B	10	5	30	200
C	10	5	30	300
I	10	20	30	100
K	20	20	30	100
M	30	20	30	100
J	10	20	60	100
L	20	20	60	100
N	30	20	60	100

Table 1

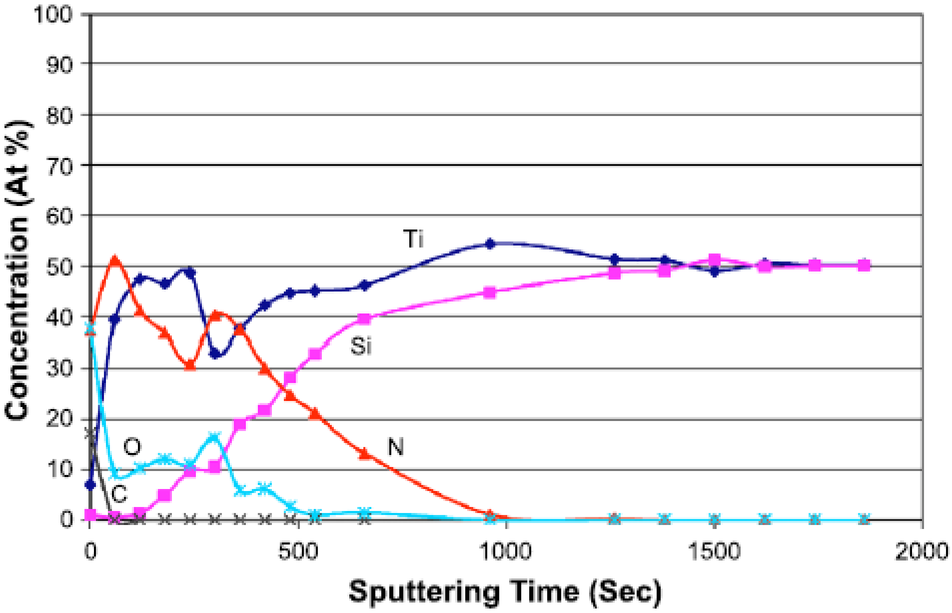

Concentration (At %)
100
90
80
70
60
50
40
30
20
10
0
Ti
Si
N
O
C
0
500
1000
1500
2000
Sputtering Time (Sec)

Figure 1

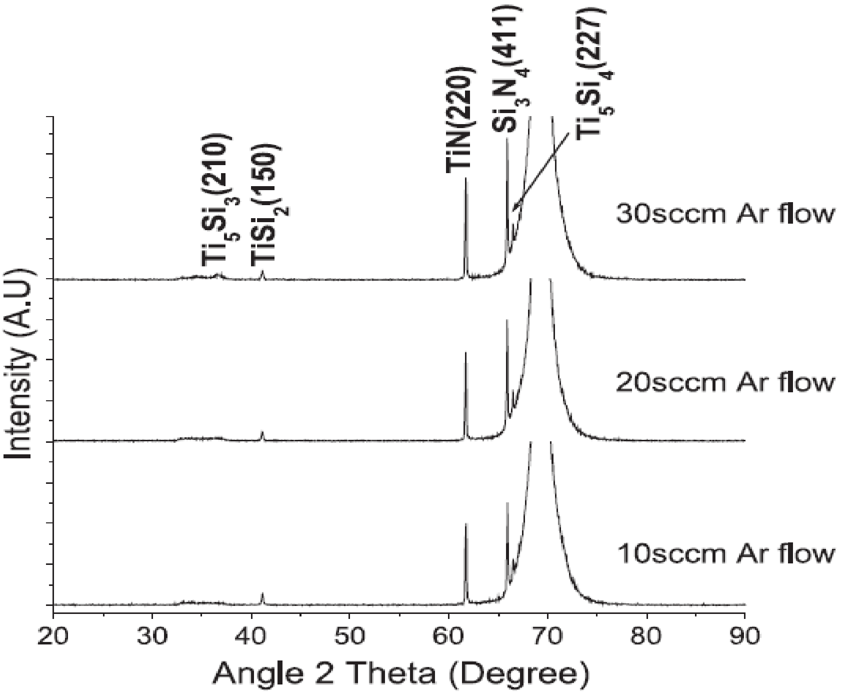

Ti$_5$Si$_3$(210)
TiSi$_2$(150)
TiN(220)
Si$_3$N$_4$(411)
Ti$_5$Si$_4$(227)
30sccm Ar flow
20sccm Ar flow
10sccm Ar flow
Intensity (A.U)
20
30
40
50
60
70
80
90
Angle 2 Theta (Degree)

Figure 2

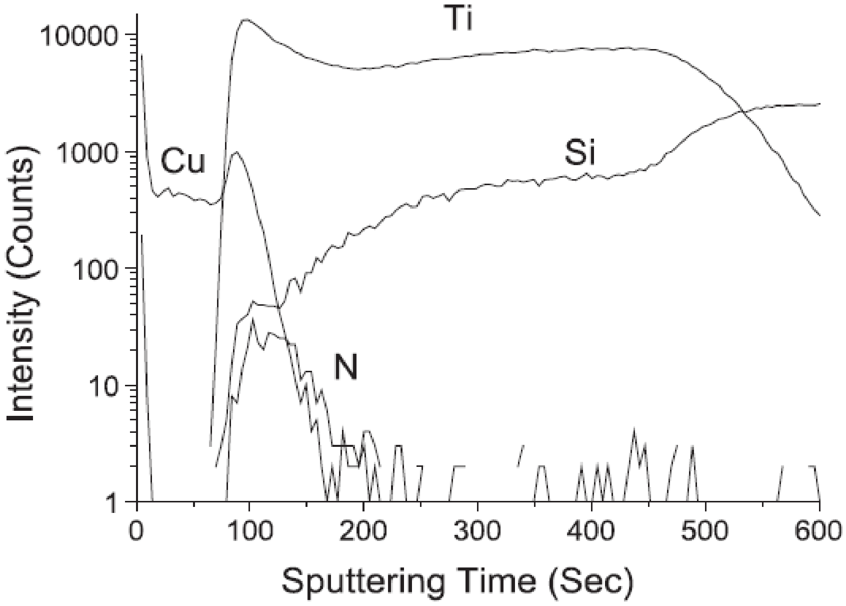

Ti
Cu
Si
N
Intensity (Counts)
10000
1000
100
10
1
0
100
200
300
400
500
600
Sputtering Time (Sec)

Figure 3

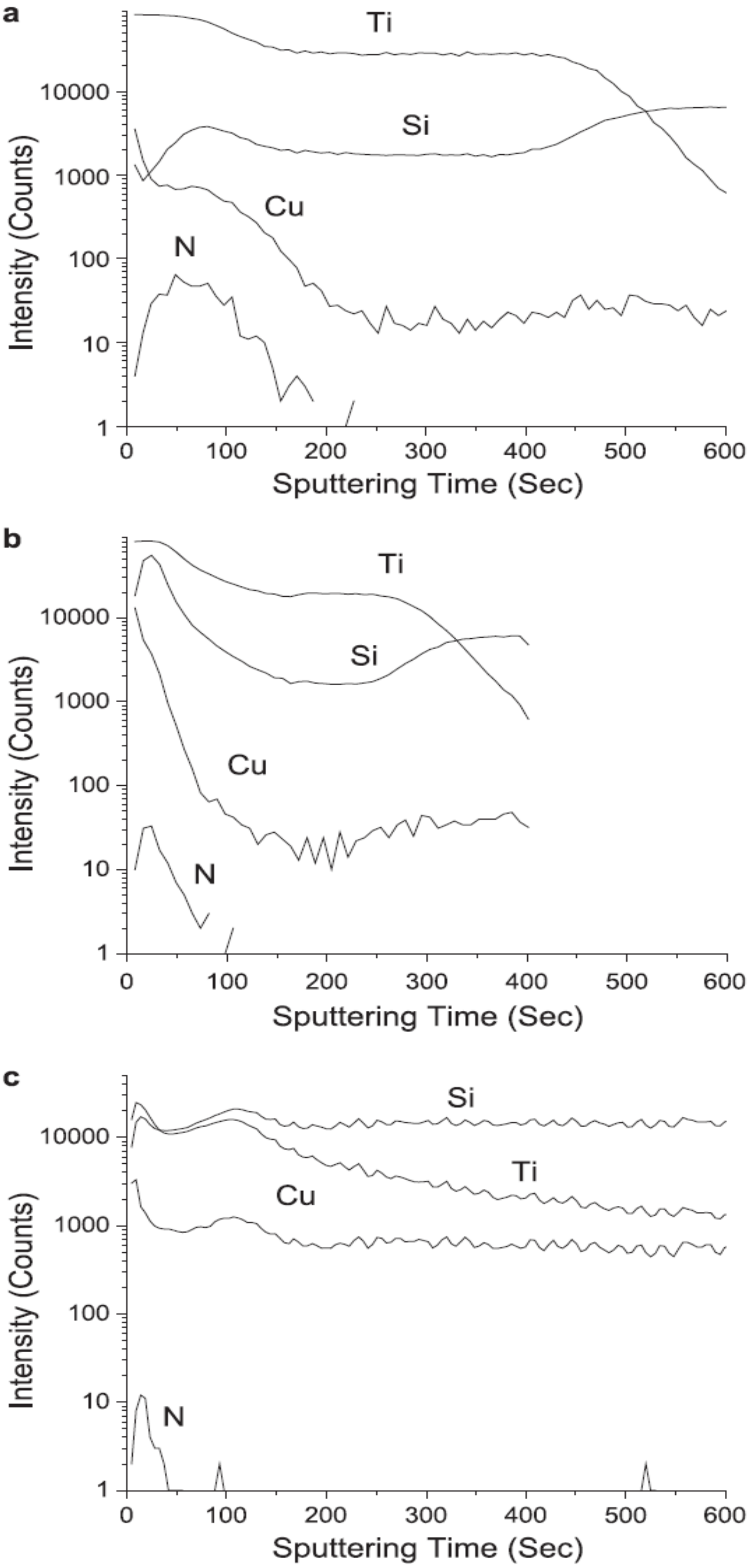
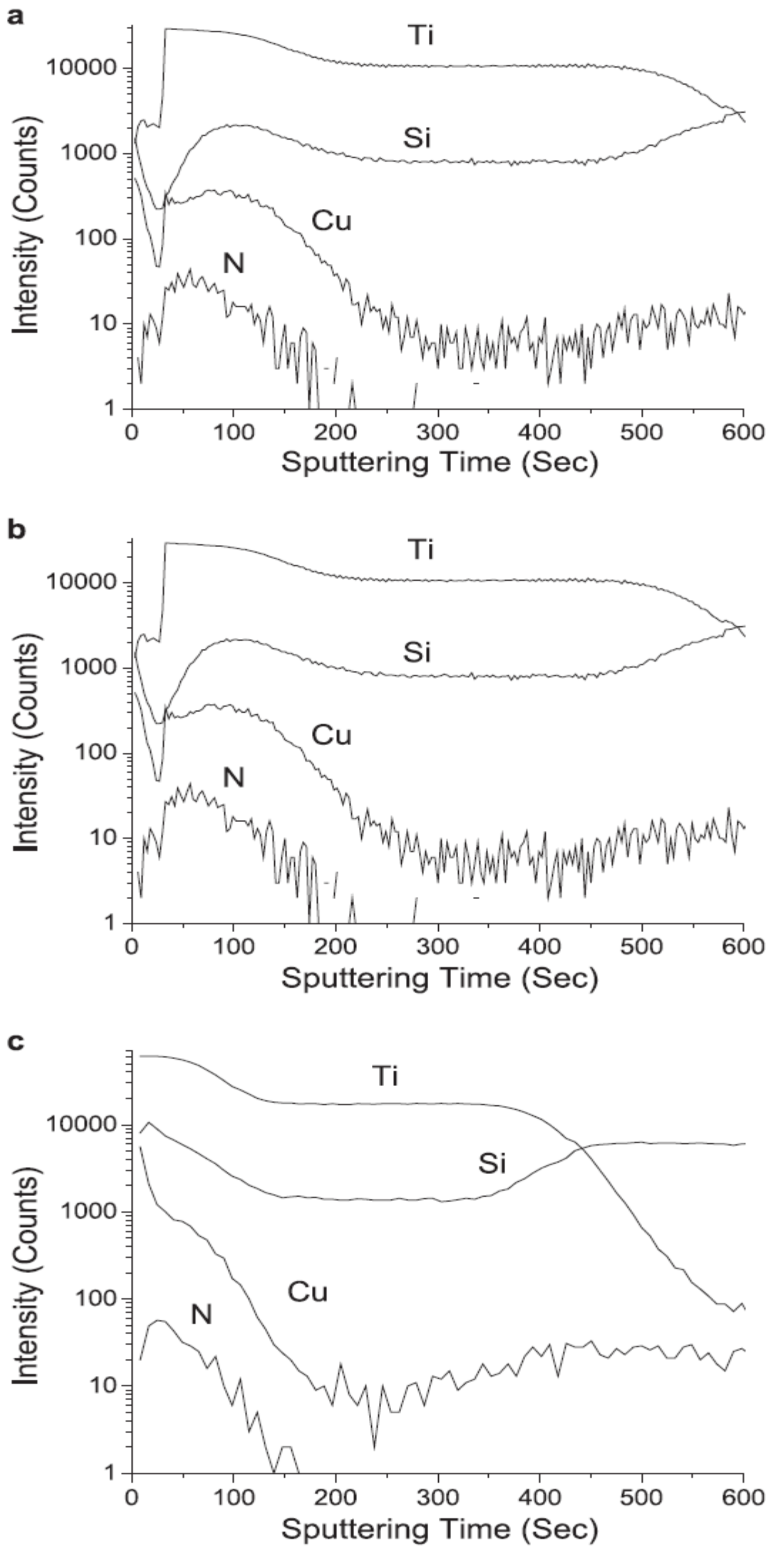

a
Ti
Si
Cu
N
Intensity (Counts)
1
10
100
1000
10000
0
100
200
300
400
500
600
Sputtering Time (Sec)
b
Ti
Si
Cu
N
Intensity (Counts)
1
10
100
1000
10000
0
100
200
300
400
500
600
Sputtering Time (Sec)
c
Si
Ti
Cu
N
Intensity (Counts)
1
10
100
1000
10000
0
100
200
300
400
500
600
Sputtering Time (Sec)

Figure 4


a
Ti
Si
Cu
N
Intensity (Counts)
10000
1000
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10
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0
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500
600
Sputtering Time (Sec)
b
Ti
Si
Cu
N
Intensity (Counts)
10000
1000
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10
1
0
100
200
300
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Sputtering Time (Sec)
c
Ti
Si
Cu
N
Intensity (Counts)
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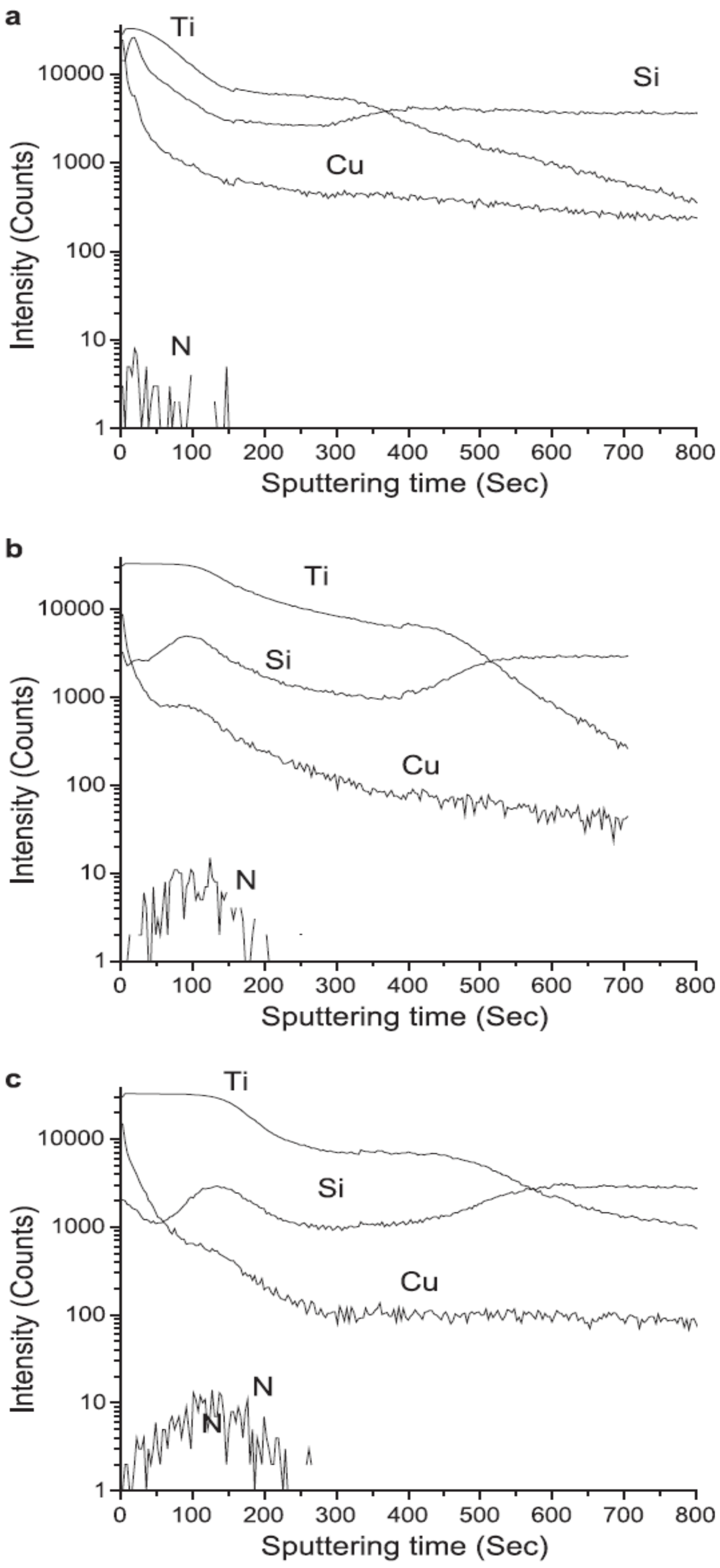
Sputtering Time (Sec)

Figure 5


a
Ti
Si
Cu
N
Intensity (Counts)
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100
1000
10000
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100
200
300
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500
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700
800
Sputtering time (Sec)
b
Ti
Si
Cu
N
Intensity (Counts)
1
10
100
1000
10000
0
100
200
300
400
500
600
700
800
Sputtering time (Sec)
c
Ti
Si
Cu
N
N
Intensity (Counts)
1
10
100
1000
10000
0
100
200
300
400
500
600
700
800
Sputtering time (Sec)

Figure 6