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Ni and Ti diffusion barrier layers between Ti-Si-C and Ti-Si-C-Ag nanocomposite coatings and Cu-based substrates

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Abstract

Sputtered Ni and Ti layers were investigated as a diffusion barrier to substitute electroplated Ni between Ti-Si-C and Ti-Si-C-Ag nanocomposite coatings and Cu or CuSn substrates. Samples were subjected to thermal annealing studies by exposure to 400 °C for 11 h. Dense diffusion barrier and coating hindered Cu from diffusing to the surface. This condition was achieved for electroplated Ni in combination with magnetron-sputtered Ti-Si-C and Ti-Si-C-Ag layers deposited at 230 °C and 300 °C, and sputtered Ti or Ni layers in combination with Ti-Si-C-Ag deposited at 300 °C.

Keywords: titanium carbide; nanocomposite; physical vapor deposition (PVD); diffusion; barrier; annealing

1. Introduction

Ceramic nanocomposite coatings have emerged as a competitive alternative to gold in electrical contact applications [1,2,3]. While others researchers have studied Ti-C-based nanocomposites with respect to tribological properties [4,5,6,7], we have focused on electrical contact properties [1,2,3,8,9,10,11] in the Ti-Si-C-based systems. Magnetron sputtered Ti-Si-C nanocomposite coatings consisting of TiC nanocrystals (nc) in a matrix of amorphous (a) SiC exhibit low contact resistance [8]. This material system has also been combined with Ag to form nc-TiC/a-SiC/Ag [9,11]. The addition of Ag results in a reduction of the electrical resistivity of the coating from 340 $\mu\Omega\text{cm}$ to 40 $\mu\Omega\text{cm}$.

Ti-Si-C and Ti-Si-C-Ag nanocomposite coatings deposited on technologically relevant Cu-alloy substrates typically suffer from Cu interdiffusion during the deposition process or operation of the contact component at elevated temperatures. Reducing the substrate temperature during, e.g., sputter deposition can, however, cause porosity [12,13] which will increase the risk of Cu diffusion to the Au contact surface. This leads to the formation of tarnish films of cuprous oxides and a degraded electrical contact performance [14]. A solution to these problems is to apply a diffusion barrier for Cu between the coating and the component. Typical diffusion barriers are electroplated Ni [15,16,17]

Here, sputtered Ni was chosen as a potential replacement of electroplated Ni. Sputtered Ti was chosen since Ti is in the contact coating and for the possibility of removing Ni altogether from the electrical contact system. Choosing sputtering as a deposition process for the barrier layers is motivated by the potential advantages in a production process if both the barrier layer and the Ti-Si-C nanocomposite coating could be deposited by sputtering.

In order to assess the functionality of the Ti-Si-C based novel electrical contact system, we compare the characteristics of Ti-Si-C and Ti-Si-C-Ag nanocomposite coatings regarding their resistance to thermal diffusion of Cu to the surface, by themselves and when combined with Ti or Ni deposited on Cu substrates. Cu has a low solubility in Ni below 400 °C [17], but can diffuse along the Ni grain boundaries, with a rate that increases with decreased grain size [18,19]. According to theory, grain boundary diffusion plays the dominant role for diffusion in polycrystalline films below $0.6 T_m$, (where T_m is the melting temperature of the material), which is the case for the present study [20]. A calculation for 2.5- μm -thick Ni according to [21] with extrapolated values from [22], gives that annealing at 400 °C during 11 h is comparable to 150 °C during 27 years, which would make for a stable contact in ambient operation conditions. Data from the literature [22,23], however, deviate as the diffusion mechanisms vary with temperature, microstructure, and chemistry of the material. This reiterates the need for a robust design. We deposited Ti-Si-C and Ti-Si-C-Ag separately onto Cu, with or without barrier layers consisting of 1) electroplated Ni or 2) sputtered Ni and 3) sputtered Ti. We find that combinations of dense Ni or Ti layers below the nanocomposite coatings are needed to hinder Cu diffusion to the surface. It can be achieved by electroplating Ni in combination with magnetron-sputtered Ti-Si-C and Ti-Si-C-Ag deposited at 230 °C and 300 °C, and sputtered Ti or Ni in combination with Ti-Si-C-Ag deposited at 300 °C.

2. Experimental details

2.1 Substrates

The substrates were made of Cu and bronze (Cu - 6 wt.% Sn) in the form of 0.5 x 5 x 5 mm coupons. Three different diffusion barrier layers were coated on both types of substrates; 2.5 μm electroplated Ni, 2 μm magnetron sputtered Ni, and 2 μm magnetron sputtered Ti. Substrates with no barrier layer were also investigated.

2.2 Electroplated diffusion barrier layers

Cu and Cu - 6 wt.% Sn substrates were cleaned with laboratory detergent (10 % Decon 90 dissolved in deionized water). Both Cu and Cu - 6 wt.% Sn substrates were then etched for 60 s with 25 g/l ammonium peroxydisulfate $((\text{NH}_4)_2\text{S}_2\text{O}_8)$, dissolved in deionized water to etch off the Cu-oxide. Any Sn oxide on the Cu - 6 wt.% Sn substrates was etched off in 20 % tetrafluoroboric acid for 30 s before electroplating.

The electroplated Ni barrier was plated at 0.8 A/dm^2 for 920 s, which gives an approximately 2.5- μm -thick layer with 100 % current efficiency according to Faraday's law in electrolysis. Table 1 shows the recipe of the electrolyte.

2.3 Sputtered diffusion barrier coatings

Ni and Ti diffusion barrier layers were deposited by magnetron sputtering in a high-vacuum industrial pilot-plant deposition system described in [9]. Ion etching with Ar was performed in the sputtering chamber on the Cu and Cu - 6 wt.% Sn substrates before sputtering in order to remove oxides from the surface. The Ni and Ti barriers were deposited during 20 min and 4.5 min respectively, without rotation of the sample, to an approximate thickness of 2 μm from elemental Ni and Ti targets, respectively, at substrate temperature of $\sim 200^\circ\text{C}$.

2.4 Deposition of top coating

Ti-Si-C and Ti-Si-C-Ag nanocomposite coatings were deposited by magnetron sputtering set to a thickness of approximately 2 μm , with rotation of the substrates and a deposition time of 2 h, in the high vacuum industrial pilot-plant deposition system mentioned above. Before deposition, ion etching with Ar was performed on the substrates in order to remove oxides. Deposition of the Ti-Si-C nanocomposite coatings was performed at two substrate temperatures, 230 $^{\circ}\text{C}$ and 300 $^{\circ}\text{C}$, from a Ti_3SiC_2 compound target (for a review of this material and the motivation for using it as target, see reference [24]). When depositing the Ti-Si-C-Ag nanocomposite coatings at substrate temperatures of 230 $^{\circ}\text{C}$ and 300 $^{\circ}\text{C}$, two sources were used; one Ti_3SiC_2 compound target and one Ag target.

2.5 Heat treatment

Heat treatment of the coated substrates was performed in a Vecstar MRF 2 furnace with a temperature control of ± 10 $^{\circ}\text{C}$ in the volume of 7.7 l at atmospheric pressure in ambient air for 11 h at 400 $^{\circ}\text{C}$. Initial tests were performed as reference at 250 $^{\circ}\text{C}$, 300 $^{\circ}\text{C}$, and 400 $^{\circ}\text{C}$ with 2.5 μm electroplated Ni as diffusion barrier layer. EDX showed no signs of Cu diffusion through the Ni at any used temperature; therefore, the highest temperature was used in the tests presented. The substrates had a temperature of approximately 20 $^{\circ}\text{C}$ when inserted into the furnace set to 400 $^{\circ}\text{C}$, and were cooled in air to room temperature after the heat treatment.

2.6 Analysis

Scanning electron microscopy (SEM) was performed in a Zeiss LEO 1550 instrument in secondary electron imaging mode with the electron beam set to 2 kV. Qualitative energy dispersive x-ray spectroscopy (EDX) analysis was used for elemental mapping of the substrate surfaces, with the electron beam set to 20 kV.

Grazing Incidence X-ray diffraction (GIXRD) scans were performed using parallel mirror on primary side, 0.27° collimator on secondary side, 45 kV, 40 mA and an Cu K α X-ray source. X-ray photoelectron spectroscopy (XPS) was performed using a Physical Electronic Quantum 2000 ESCA Microprobe. The sputtering profiles were performed by 21 cycles of 3 min sputtering each, using Ar⁺ and 4 keV over a surface of $2 \times 2 \text{ mm}^2$, analysis area was 200 μm in diameter. Cross-sectional Transmission electron microscopy (TEM) samples was prepared using a Zeiss 1540 EsB CrossBeam FIB using the lift out technique described in [25]. TEM images and EDX in scanning TEM (STEM) mode was performed with a Tecnai G² 20 U-Twin 200 kV FEGTEM.

3. Results

3.1 As-deposited coatings

The as-deposited coatings exhibited no traces of Cu on the surface as seen by SEM and EDX analyses. Therefore, no Cu diffused to the surface during deposition or storage in air of the samples.

Figure 1 shows GIXRD $\theta/2\theta$ scans from a Ti-Si-C-Ag nanocomposite coating deposited at 300°C on substrates consisting of a) sputtered Ni on Cu – 6 wt. % Sn, b) Cu, c) electroplated Ni on Cu, and d) sputtered Ti on Cu. In Figure 1, there are peaks from the substrate and respective barrier layer a) CuSn and Ni, b) Cu, c) Cu and Ni, and d) Cu and Ti, while TiC and Ag peaks from the only crystalline phases in the Ti-Si-C-Ag coatings are present in all scans. CuO found is also present in b), indicating that the nanocomposite coating is porous allowing O to diffuse to the Cu forming CuO. Substrate and barrier layers show sharp, high-intensity peaks indicating large crystal sizes in the substrates, electroplated Ni, sputtered Ni, and Ti layers. The peaks from TiC and Ag are broad and of low intensity indicating a nanocrystalline growth behavior of both the carbide and the Ag,

which is in accordance with [9,11]. GIXRD scans of Ti-Si-C show the same result as for Ti-Si-C-Ag substrates except for the lack of Ag peaks, with high-intensity peaks from the substrates and barrier layers, while the TiC peaks are broad and have low intensity, indicating nanocrystalline growth similar to [8,10].

XPS were performed to verify that the coatings have the TiC/SiC/Ag characteristics [9,11]. XPS spectra of Ti-Si-C coatings show C1s peak at 282.5 eV with a broadening of the peak to 281.8 eV from the presence of C-Si and C-Ti bonds. The peaks of Ti2p_{3/2} at 455 eV and Ti2p_{1/2} at 461 eV indicate that the Ti is chemically bonded to C as Ti-C [26,27], and the Si2s peak at 151.8 eV corresponds to Si-C bonds [28]. Ag3d spectra cannot provide information regarding the presence of Ag-Si bond in the coating, since there is no significant peak shift or broadening regarding transition from Ag-Ag bonds to Ag-Si bonds [29]. Mixing in the Ag-Si system is known to be very limited, without formation of metastable phases up to 400 °C [29,30].

The Ti-Si-C-Ag coating has a C1s peak at 282.5 eV broadening to 281.8 eV again from C-Si and C-Ti bonds, and Ti2p_{3/2} found at 455.1 eV indicate Ti-C bonds. A peak at 151 eV in-between the peaks for Si-Si and Si-C bonds suggests the presence of both these bonds. The presence of Ag-Ag bonds is demonstrated by Ag3d_{5/2} and peaks at 368.5 eV. These XPS spectra of both Ti-Si-C and Ti-Si-C-Ag are thus in agreement with previous studies by Eklund et al. and Lauridsen et al. [8,9,10,11].

Figure 2 shows cross-sectional a) TEM image of the Ti-Si-C-Ag/Ni interface and b) STEM image with corresponding EDX elemental maps of the sputtered Ni/Cu interface, of Ti-Si-C-Ag deposited at 300 °C on sputtered Ni. The Ti-Si-C-Ag coating has a homogeneous nanocomposite structure with essentially equiaxed TiC and Ag grains, and the sputtered Ni

coating is found to be polycrystalline with a columnar structure. No Cu can be seen to diffuse into the Ni at the Ni/Cu interface in the as-deposited samples.

In summary; analyses show that the as-deposited coatings are Ti-Si-C nanocomposites consisting of TiC nanocrystals in a matrix of amorphous SiC, and Ti-Si-C-Ag nanocomposites with TiC and Ag nanocrystals in an amorphous matrix with Si-Si and Si-C bonds. This agrees well with previous work on Ti-Si-C and Ti-Si-C-Ag [8,9,10,11].

3.2 Heat treatment

Figure 3 shows GIXRD $\theta/2\theta$ scans of the Ti-Si-C-Ag nanocomposite coatings deposited at 300 °C, after heat treatment at 400 °C for 11 h for the cases of deposition on a) sputtered Ni on Cu – 6 wt. % Sn, b) Cu, c) electroplated Ni on Cu, and d) sputtered Ti on Cu.

The diffractograms have peaks from the substrate material and barrier layers, as well as peaks from TiC and Ag. No phases other than those present in the as-deposited samples can be identified after heat treatment in GIXRD scans of Ti-Si-C (with and without Ag) deposited on barrier layers or substrates. The fact that no CuO is found in Figure 3 b), indicate that the heat treatment allow Cu and Ag to diffuse in the nanocomposite making it denser and the hindering O from diffusing down to the Cu. At the same time the as-deposited coating will remain porous allowing O to diffuse down to the Cu forming more CuO.

Figure 4 shows an a) SEM image and b) corresponding Cu-K EDX map of the Ti-Si-C-Ag nanocomposite coating deposited at 300 °C on a Cu substrate after annealing at 400 °C for 11 h. Figure 4 show that Cu has diffused to the surface of the coatings, with an ~60 % coverage. Such Cu diffusion behavior is representative also for Ti-Si-C and Ti-Si-C-Ag

nanocomposite deposited at 230 °C and 300 °C directly on Cu and Cu - 6 wt.% Sn substrates (result not shown).

Figure 5 presents samples annealed at 400 °C for 11 h; a) SEM image and b) Cu-K EDX Cu map of Ti-Si-C deposited at 230 °C on electroplated Ni, c) SEM image, and d) EDX Cu map of Ti-Si-C-Ag deposited at 300 °C on sputter-coated Ti as well as e) SEM image and f) EDX Cu map of Ti-Si-C-Ag samples deposited at 300 °C on sputter-coated Ni, all deposited on Cu substrates. The EDX maps reveal an even distribution of Ti, Si, C, and Ag. No indications of Cu diffusion (spots) could be found using SEM and EDX on any of the coatings deposited on electroplated Ni substrates. Also, the Ti-Si-C-Ag deposited at 300 °C on Cu or Cu - 6 wt. % Sn substrates using sputtered Ti or Ni show no Cu on the surface.

Figure 6 shows a) SEM image and b) corresponding Cu-K EDX map of a diffusion spot formed during annealing of the Ti-Si-C nanocomposite deposited at 300 °C on a Cu substrate with a sputtered Ni diffusion barrier layer. The sample exhibits Cu diffusion to the surface of the coatings with roughly 10 diffusion spots per mm² after annealing, which is much less than when the nanocomposites are deposited directly onto the Cu substrate, where Cu can be seen almost over the whole surface, see Figure 4. The appearance of the diffusion spot in Figure 6 is typical for pore-corrosion [31,32] where Cu by surface diffusion transports through the pore up to the surface with Cu oxidation as a driving force. After annealing of Ti-Si-C nanocomposites deposited at 230 °C on Ni-sputtered Cu substrates, Cu had diffused to the surface of the coatings and was found all over the surface, but to a much less extent than when using no barrier coating. Ti-Si-C-Ag nanocomposites deposited at 230 °C on Ni sputtered Cu substrate showed diffusion of Cu to the surface with roughly 10 diffusion spots per mm².

Figure 7 shows SEM images of samples after heat treatment at 400 °C during 11 h: a) Ti-Si-C nanocomposite deposited at 300 °C and b) Ti-Si-C-Ag nanocomposite deposited at 300 °C, both coatings deposited on Ti-sputtered Cu substrates. It can be seen that Cu has diffused to the surface of the Ti-Si-C to form bright spots, while no spots are seen on the Ti-Si-C-Ag surface. This indicates that the introduction of Ag to the Ti-Si-C coating results in an increased resistance against Cu diffusion.

Figure 8 shows an XPS sputtering depth profile of the Ti-Si-C nanocomposite coating deposited at 300 °C on Cu substrate, after heat treatment. Cu is found both at the surface and inside of the coating. The surface spectra differ from those further down in the coating and agree well with references of CuO [33]. The spectra obtained from inside of the coating are less oxidized, but due to potential sputter damage on CuO [34] the oxidation state of the Cu cannot be determined. However, the presence of CuO is expected since Cu₂O preferentially forms at relatively low temperatures [35]. Moreover, there is a region just below the surface where less Cu is observed than on the surface or into the coating and which contains Ti-O and Si-O bonds. No Cu was found on the surface or inside of the annealed Ti-Si-C-Ag coatings deposited at 300 °C on Ni sputtered Cu substrate.

Figure 9 shows cross-sectional TEM images of the a) Ti-Si-C-Ag/Ni and b) Ti-Si-C/Ni interfaces after heat treatment at 400 °C during 11 h, with the nanocomposites deposited at 300 °C. The Ti-Si-C coating has a pronounced columnar structure stemming from competitive growth. The Ti-Si-C-Ag coating instead has a homogeneous nanocomposite structure with equiaxed TiC and Ag grains. The sputtered Ni coating is polycrystalline with a columnar structure. There is no change in structure of the coatings after heat treatment (c.f. Fig 2).

Figure 10 shows STEM cross-sectional images with corresponding EDX elemental maps from the interface regions of a) Ti-Si-C/Ni and b) Ni/Cu with Ti-Si-C deposited at 300 °C, after heat treatment at 400 °C during 11 h. Cu has diffused massively into the Ni through grain boundaries (c.f. Figure 9 b), during the heat treatment. At the interface of Ti-Si-C/Ni in Figure 10 a), the massive Cu diffusion seems to stop or slow down at the interface while the Ni diffuses into the Ti-Si-C along the columns close to the interface. No Ni was found beyond ~400 nm into the Ti-Si-C coating.

Figure 11 shows cross-sectional STEM images with corresponding EDX elemental maps performed after heat treatment, showing the interface regions of a) Ni/Cu, b) Ti-Si-C-Ag/Ni, c) enlarged elemental maps of Ag and Cu in a), where the nanocomposite coating was deposited at 300 °C. During heat treatment, Ni diffuses approximately 150-200 nm into the Ti-Si-C-Ag while Cu diffuses into the Ti-Si-C-Ag coating to a small extent, and is preferentially located to the Ag grains, see Figure 11 c. Finally, the annealed samples exhibit voids, ranging in size up to 200 nm in the Ni layer next to the Ni/Cu interface (see Figures 10 and 11), with a lower amount of voids at the Ti-Si-C-Ag/Ni and Ti-Si-C/Ni interfaces, respectively.

4. Discussion

Replacing Au contacts with Ti-Si-C based contacts requires the replacement of the whole contact system with contact coating, diffusion barrier and the electrical conductive substrate. The results show that, in order to hinder Cu from reaching the surface through the Ti-Si-C and Ti-Si-C-Ag nanocomposite coating combinations, there is a need for a dense diffusion barrier layer. Commonly, Ni-plated coatings are used as diffusion barriers, but they need to be deposited thick enough to seal the coating in order to function as a diffusion barrier. Plated Ni is often deposited with a thickness of 1.25-2.5 [36] for

diffusion barrier applications. This barrier layer is deposited between the Ti-Si-C (with or without Ag) nanocomposite coatings and the Cu or Cu - 6 wt.% Sn substrates. The driving force for Cu diffusion is besides entropy gain the presence of oxygen, causing the Cu to oxidize. Cu is known to oxidize well below 400 °C [37], and increased temperature accelerates the diffusion process.

When no barrier layer is deposited between top coating and substrate, diffusion (Figure 4) of Cu in the top coatings seems to preferentially occur through the amorphous matrix of the nanocomposite. This diffusion path is expected since the diffusion is faster in amorphous compounds than in crystals [20].

Electroplated Ni as diffusion layer between Ti-Si-C (with or without Ag) nanocomposite coatings and Cu or Cu – 6 wt.% Sn substrates, can hinder Cu from diffusing to the surface. Independent of deposition temperature of the nanocomposite coatings, the Cu is hindered to reach the surface when using the electroplated Ni as diffusion layer during annealing at 400 °C. This implies that the electroplated Ni layer has a dense microstructure.

When applying sputtered Ni or Ti layers between Cu or Cu – 6 wt. % Sn substrates and top coating, Cu diffuses through the sputtered Ti and Ni to the top coating. However, in combination with Ti-Si-C-Ag deposited at 300 °C, Cu can be hindered from diffusing to the surface during annealing at 400 °C for 11 h. The interdiffusion of Cu to the surface is dependent on the microstructure of Ti-Si-C-Ag deposited on sputtered Ni or Ti, and the microstructure is affected by the coating deposition temperature. Ti-Si-C-Ag deposited at 300 °C on Ti or Ni sputtered Cu or Cu – 6 wt. % Sn substrates, hinder diffusion of Cu to the surface during annealing, and thus the coating combination functions as a diffusion

barrier. While this is not the case for same combination with Ti-Si-C-Ag deposited at 230 °C.

Sputtered Ti or Ni layers between Ti-Si-C (independent on deposition temperature) and Cu or Cu – 6 wt. % Sn substrates, do not hinder Cu from diffusing through the coating combination to the surface, during annealing. Diffusion spots on the surface as seen in Figure 6 a) and b) indicate that Cu diffusion occurs through pores or other defects in the sputtered diffusion barrier and top coating. However, the pores are too far apart to be seen in TEM.

Deposition by electroplating of Ni is driven by a potential attracting the Ni ions and depositing Ni as metal on the surface, and in this case the coating has a leveling effect of the coating. This means that defects, pores and irregularities will be sealed during deposition, and the coating will be dense and smooth due to the process. DC sputtering as a process can have problems of sealing pores or defects especially if there is columnar growth stemming from competitive growth as here for sputtered Ni and Ti. Increased surface diffusion is desired to get denser coatings with DC sputtering, and one way is to increase the substrate temperature relative to the melting point of relevant element, resulting in denser coating. In present case it is, however, desired to keep the coating temperature low, in order to not anneal the cold hardened Cu, which commonly is used in contact applications, reducing the material properties when annealing at temperatures around 300 °C for longer periods of time.

The amount of Cu interdiffusion to the surface was shown to be much lower for Ti-Si-C independent of deposition temperature and Ti-Si-C-Ag deposited at 230 °C, all coated on Cu or Cu - 6 wt.% Sn substrates with sputtered Ni and Ti barrier layers, when compared to not using any barrier layers, as can be seen in Figure 4. This shows that the sputtered Ti

and Ni coatings are not sufficient to hinder Cu from diffusing to the surface (c.f. Figure 10 and 11).

As seen in Figures 9-11, the addition of Ag to the Ti-Si-C nanocomposite coatings deposited at 300 °C does not only improve the electrical properties [9,11], but it also yields a nanocomposite coating, which seems to be resistant to pore diffusion. Figure 9 shows that the Ti-Si-C has a columnar structure (as expected [8,10]), while the Ti-Si-C-Ag has an equiaxed structure. This difference is likely to contribute to faster diffusion in the case of Ti-Si-C with columnar structure. Smaller crystal size as the case for Ti-Si-C-Ag on other hand leads to a more isotropic diffusion through the amorphous matrix and grain boundaries as can be seen for Ni in Figure 11 b). The rough Cu substrate surface can result in pores or under dense grain boundaries in the sputtered Ti and Ni, which becomes sealed when depositing Ti-Si-C-Ag at 300 °C on the sputtered Ti and Ni. For corresponding deposition directly on to the rough Cu substrate, the initial growth can result in pores or under dense grain boundaries due to insufficient adatom mobility. Instead, the higher deposition temperature of Ti-Si-C (with or without Ag) leads to a denser coating [12,13], and thus the amount of Cu interdiffusion becomes less for both coatings when deposited on Ti and Ni sputtered Cu or Cu - 6 wt. % Sn substrates. The Ti-Si-C coating becomes denser at higher temperatures as expected, but the core problem with columnar structure stemming from competitive growth still do not seal pores and defects to an satisfactory level for hindering Cu diffusion to the surface. Since Ag has a lower melting temperature than Ti, Si, and C, it has a higher mobility during deposition, making it more likely to fill in structural irregularities, with an increased efficiency at the higher deposition temperature. Ag has also the impact of hindering TiC crystal growing too large, but do allow renucleation of TiC crystals leading to a coating with equiaxed TiC and Ag crystals in a amorphous matrix with Si-Si and Si-C. These effects of the Ag in the Ti-Si-C coating

result in sealing of pores and defects to such extent that Cu is hindered from diffusing to the surface. Changing the deposition parameters in order to change the surface roughness and microstructure of the different layers as made in [38] to get a denser coating would be a very interesting continuation of this work, but in this paper we have focused on using coating parameters tuned for a functional low contact-resistance coating.

Ag competes with Cu for the diffusion paths in the nanocomposite during annealing, thus restricting Cu from diffusing to the surface. The Ag, however, has less diffusion-driven force to the surface from oxidation, since Ag_2O decomposes at temperatures below 400 °C [32]. As a matter of fact, we find the Cu is preferentially located to the Ag grains (Figure 11 c). The phase diagram of Cu and Ag [39] at 400 °C shows that there is a solid phase of Ag with a limited solubility for Cu. It is therefore likely that during the annealing at 400 °C some Cu segregate with the Ag solid phase. Thus, Ti-Si-C-Ag deposited at 300 °C on sputtered Ni or Ti, are functional coating combinations that hinder Cu from diffusing to the surface when deposited on Cu substrates.

5. Conclusions

Sputtered Ni or Ti layers in combination with dense Ti-Si-C-Ag contact coatings function as a Cu diffusion barrier at 400 °C during 11 h. It is possible to deposit both barrier and top coating in the same production system at temperatures not exceeding 300 °C. Dense electroplated Ni diffusion barrier layers may thus be substituted, which offers an advantage for contact applications. Cu diffusion in Ti-Si-C-Ag is preferentially located to the Ag grains. Nickel diffuses into the Ti-Si-C films preferentially along the columns, while it has a more isotropic diffusion into the amorphous Si-Si and Si-C matrix of Ti-Si-C-Ag coatings.

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Tables

Table 1. Recipe of Ni sulfamate electrolyte.

Nickel sulfamate	$\text{Ni}(\text{NH}_2\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$	310 g/l
Nickel chloride	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	31 g/l
Boric acid	H_3BO_3	31 g/l
BP-N1	$\text{C}_{10}\text{H}_8\text{O}_9\text{S}_3 \cdot 3\text{Na} \cdot x\text{H}_2\text{O}$	6.2 g/l
Sodium dodecyl sulfate	$\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$	0.25 g/l

Figure captions

Figure 1. GIXRD scans of as-deposited Ti-Si-C-Ag nanocomposite top coatings deposited at 300 °C sputtered on a) sputtered Ni barrier layer on Cu – 6 wt. % Sn, b) Cu, c) electroplated Ni barrier layer on Cu, and d) sputtered Ti barrier layer on Cu.

Figure 2. Cross-sectional views of a) an as deposited Ti-Si-C-Ag coating deposited at 300 °C on a sputtered Ni layer imaged by TEM and b) the corresponding Ni/Cu substrate interface image by STEM with EDX elemental maps (inserts).

Figure 3. GIXRD scans from Ti-Si-C-Ag nanocomposite top coatings deposited at 300 °C sputtered on a) sputtered Ni on Cu – 6 wt. % Sn, b) Cu, c) electroplated Ni on Cu, and d) sputtered Ti on Cu, after heat treatment in 400 °C for 11 h.

Figure 4. a) SEM image, and b) corresponding Cu-K EDX map of Ti-Si-C-Ag nanocomposite deposited at 300 °C on Cu substrate coated surface after heat treatment at 400 °C during 11 h.

Figure 5. Images of coated surfaces after heat treatment at 400 °C during 11 h in: a) SEM image and b) corresponding Cu-K EDX map on Ti-Si-C nanocomposite deposited at 230 °C on Ni electroplated Cu substrate; and c) SEM image and d) corresponding Cu-K EDX map of Cu on Ti-Si-C-Ag nanocomposite deposited at 300 °C on Ti sputtered Cu - 6 wt.% Sn substrate; and e) SEM image and f) corresponding Cu-K EDX map of Cu on Ti-Si-C-Ag nanocomposite deposited at 300 °C on Ni sputtered Cu - 6 wt.% Sn substrate.

Figure 6. a) SEM image and b) corresponding Cu-K EDX map, after annealing at 400 °C during 11 h of Ti-Si-C nanocomposite deposited at 300 °C on Ni sputtered Cu substrate.

Figure 7. SEM images of top coatings consisting of a) Ti-Si-C nanocomposite deposited at 300 °C, and b) Ti-Si-C-Ag nanocomposite deposited at 300 °C, onto Ti sputtered Cu substrates, after heat treatment at 400 °C during 11 h.

Figure 8. XPS spectra of the Cu2p region from a depth profile of Ti-Si-C nanocomposite coating deposited at 300 °C on a Cu substrate, after heat treatment at 400 °C during 11 h, with scans recorded after each sputter cycle from 0 (as –deposited) to 20.

Figure 9. Cross-sectional TEM images from a) Ni/Ti-Si-C-Ag and b) Ni/Ti-Si-C interfaces, after heat treatment at 400 °C during 11 h, of sample with nanocomposite top coatings sputtered at 300 °C on sputtered Ni barrier layer on Cu.

Figure 10. Cross-sectional STEM images with corresponding EDX elemental maps from the a) Ti-Si-C/Ni and b) Ni/Cu interfaces, after heat treatment at 400 °C during 11 h, of a sample with Ti-Si-C nanocomposite top coating sputtered at 300 °C on sputtered Ni barrier layer on Cu.

Figure 11. Cross-sectional STEM image with corresponding EDX elemental maps showing interfaces from a) Ti-Si-C-Ag/Ni, b), Ni/Cu and c) enlarged EDX elemental maps of Ag and Cu from b) with grains containing both metals encircled, after heat treatment at 400 °C during 11 h, of a sample with Ti-Si-C-Ag nanocomposite top coating sputtered at 300 °C on sputtered Ni barrier layer on Cu.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Highlights

Investigation of Cu diffusion barriers in Ti-Si-C based nanocomposite contacts.

Sputtered Ni or Ti layers combined with Ti-Si-C-Ag coatings can hinder Cu diffusion.

Cu diffusion can be hindered combining electroplated Ni with Ti-Si-C or Ti-Si-C-Ag.