# Films of Ni–7 at% V, Pd, Pt and Ta–Si–N as diffusion barriers for copper on Bi$_2$Te$_3$

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**Abstract.** Films of Ni–7 at% V, Pt, Pd, and Ta$_{40}$Si$_{14}$N$_{46}$, each approximately 100 nm thick, were magnetron-deposited and interposed between about 250 nm thick copper overlayers and Bi$_2$Te$_3$ single-crystalline substrates. The samples were then annealed in vacuum up to 350 °C. The performance of the metal and the tantalum-silicon-nitride films as diffusion barriers for in-diffusion of Cu and out-diffusion of Bi and Te was evaluated by 2.0 MeV $^4$He backscattering spectrometry and x-ray diffraction. The Ni–7 at% V, Pd and Pt films all fail to prevent interdiffusion of Cu and Bi$_2$Te$_3$ after a few hours of annealing at 200 °C. However, the Ta$_{40}$Si$_{14}$N$_{46}$ barrier preserves the integrity of the contact after 250 °C for 50 h and 350 °C for 1 h anneals. These results confirm the superior characteristics of the metal-silicon-nitride films as diffusion barriers.

## 1. Introduction

Increasing power levels and packaging densities are necessary to improve the processing speed as well as the functional density of integrated circuits. The next generation of solid state power electronics is expected in a few years time to generate as much as 30 W of heat within a single chip [1]. This increase means that advanced thermal management techniques capable of handling heat fluxes of several hundred W cm$^{-2}$ must be developed. One way to manage such thermal fluxes is to use thermoelectrical microcoolers for spot cooling of sensitive electronic components. The main performance advantage of miniature thick-film thermoelectrical cooling devices over conventional bulk thermoelectrical modules is their ability to increase the cooling power density because the cooling power per unit area is inversely proportional to the thickness of the thermoelectrical legs.

As a bulk material, the thermoelectrical intermetallic compound Bi$_2$Te$_3$ and its alloys are widely used in refrigerators, thermostats and piezo-electrical devices [1]. Details about the deposition of thick Bi$_2$Te$_3$ films and the development of bismuth-telluride-based spot cooling devices have been reported elsewhere [2, 3]. For Bi$_2$Te$_3$-based thermoelectrical devices, copper is a desirable choice as a metallic electrode, because it has high thermal conductivity and low electrical resistivity. On the other hand, Cu exhibits donor activity in Bi$_2$Te$_3$ and is known for its high diffusivity in bismuth telluride and the formation of Cu$_2$Te [1]. Because the soldering temperatures of thermoelectrical devices are typically about 200 °C

and the operating temperatures are up to about 100 °C, the deployment of a chemically inert and low-resistivity diffusion barrier between the Cu metallization overlayer and the thermoelectrical base material is indispensable. Traditionally, Ni has been employed as the barrier material of choice for bulk thermoelectrical (or Peltier) cooling devices [4].

In recent years, copper has also attracted attention in the technology of very-large-scale integrated circuits, as a possible replacement for aluminium as an interconnection material. Compared to aluminium, Cu has a lower resistivity and superior stability against void formation and electromigration [5–7]. A critical issue in this application is to avoid the diffusion of Cu or Al into the silicon. When it is used as a barrier material between Cu and Si, TiN is stable up to a maximum temperature of 650 °C [8]. In contrast, no failures up to temperatures of 850 °C were observed with amorphous, or nano-crystalline, transition-metal silicon nitrides such as Ti–Si–N and Ta–Si–N [9, 10]. These ternary materials adequately fulfil the requirements of the electrical bulk and contact resistivity that a diffusion barrier must satisfy in this application. For 100 nm thick Ti–Si–N films, resistivity values of about 300 $\mu\Omega$ cm at room temperature and about 700 $\mu\Omega$ cm at 850 °C were measured [9]. These values are to be compared with about 7 $\mu\Omega$ cm for Ni and 10 $\mu\Omega$ cm both for Pd and for Pt near room temperature. In this paper we report on the effectiveness of metal films of Ni–7 at% V, Pt and Pd and Ta$_{40}$Si$_{14}$N$_{46}$ films as diffusion barriers at temperatures up to 350 °C for Cu overlayers on bulk single-crystalline Bi$_2$Te$_3$ substrates.

## 2. Experimental details

$Bi_2Te_3$ crystals were grown using the gradient freeze technique. A vertical two-zone furnace was used with a thermal baffle introduced between the upper and the lower zone in order to prevent air convection. Details about the furnace were reported elsewhere [11]. The bismuth-telluride growth was conducted in a sealed quartz ampoule. Bi and Te (99.999 at% purity) were introduced into the quartz ampoules in quantities corresponding to the $Bi_2Te_3$ stoichiometry, sealed under vacuum and heated up to $600\,°C$. The growth process was then carried out by lowering the temperature of the furnace at a cooling rate of about $0.7\,°C\ h^{-1}$. The temperature difference between the upper (hotter) and lower (colder) zones of the furnace was maintained, giving a temperature gradient of about $50\,°C\ cm^{-1}$ at the interface. Ingots (about 6 cm long and about 1 cm in diameter) were obtained, cleaved along the planes perpendicular to the $c$ axis of the hexagonal crystal and then cut into samples of about $0.5\ cm^2$ surface area. The stoichiometry of the samples was measured by electron probe microanalysis and found to be close to $Bi_2Te_3$ composition (to within $\pm0.2$ at%). Additional backscattering spectrometry confirmed these atomic concentrations (to within $\pm2$ at%).

The metal and Ta–Si–N thin films were deposited onto the $Bi_2Te_3$ substrates by rf magnetron sputtering in a cryo-pumped system of $2 \times 10^{-7}$ Torr base pressure. The 7.5 cm diameter sputtering targets of Ni–7 at% V, Pt and Pd were of 99.999 at% purity. Vanadium was added to the Ni to make the target non-magnetic. The sputtering gas was argon. For the Ta–Si–N deposition, a $Ta_5Si_3$ target of 99.995 at% purity was reactively sputtered in an argon–nitrogen plasma. The sample holder was neither cooled nor heated during deposition. We estimate that the sample temperature remains below about $100\,°C$. The thickness of the deposited films is in the range of $100 \pm 15$ nm. Without breaking the vacuum a copper overlayer of about $250 \pm 50$ nm thickness was subsequently deposited. For all depositions, the total gas pressure was 10 mTorr and the forwards rf power was 300 W. The samples were annealed in an oil-pumped vacuum of $6 \times 10^{-7}$ Torr at 200 and $350\,°C$ for durations of 50 and 1 h, respectively.

The thicknesses of the as-deposited films were measured with a step profilometer. Elemental depth profiles before and after annealing were obtained by 2.0 MeV $^4$He backscattering spectrometry. All backscattering analyses were performed with an angle of incidence of the $^4$He beam of $7°$ from the sample normal and an angle of $170°$ for the detected particles. The spectra were fitted with the RUMP89 simulation code for quantification of the stoichiometry [12]. The composition of the tantalum-silicon-nitride film determined by this technique was $Ta_{40}Si_{14}N_{46}$. Backscattering spectra of films on carbon substrates revealed oxygen and argon as contaminants, both in concentrations of about 2 at%.

In figures 1(a) and 1(b), the backscattering spectra of the as-deposited $Bi_2Te_3/Ta–Si–N(100\ nm)/Cu(220\ nm)$ and $Bi_2Te_3/Pt(90\ nm)/Cu(280\ nm)$ samples are plotted, together with fits obtained with RUMP89 for the
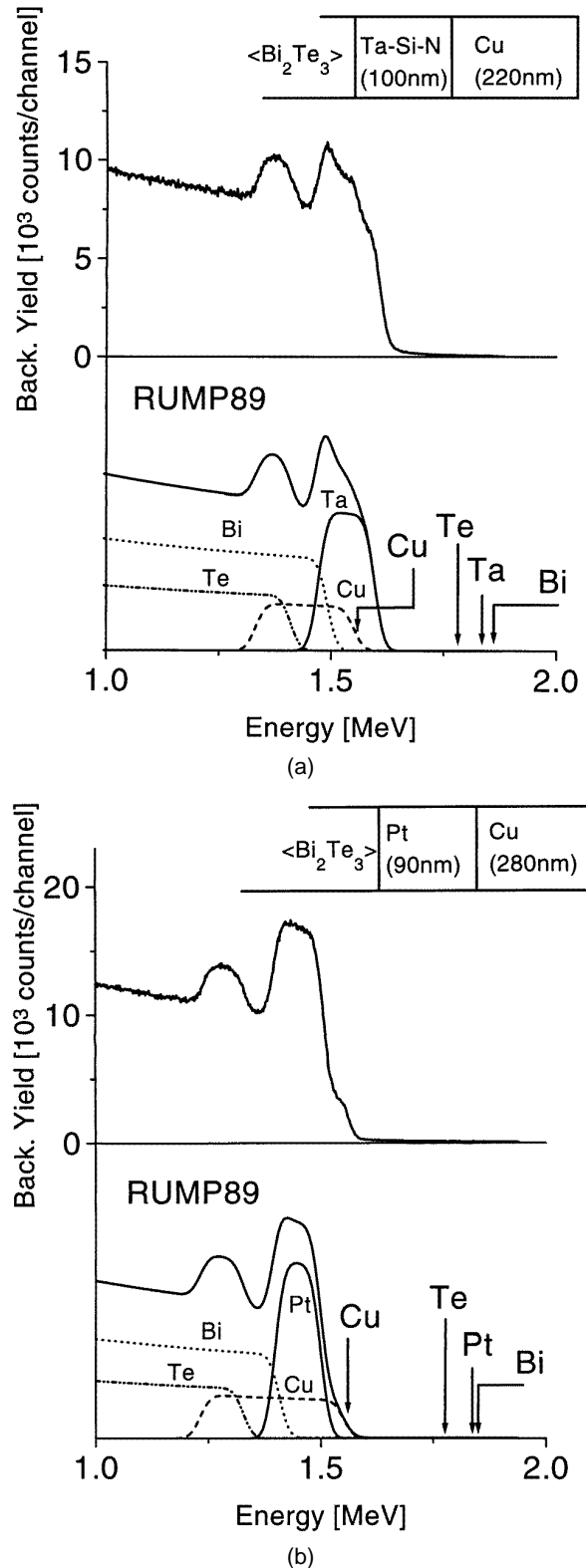


**Figure 1.** 2.0 MeV $^4$He backscattering spectra of as-deposited $Bi_2Te_3/Ta_{40}Si_{14}N_{46}(100\ nm)/Cu(220\ nm)$ (a) and $Bi_2Te_3/Pt(90\ nm)/Cu(280\ nm)$ (b) samples, together with the RUMP89 computer code calculated total yields and the single-component yields. The backscattering surface energies of Bi, Te, Cu and Ta or Pt respectively are marked on the abscissa by arrows.
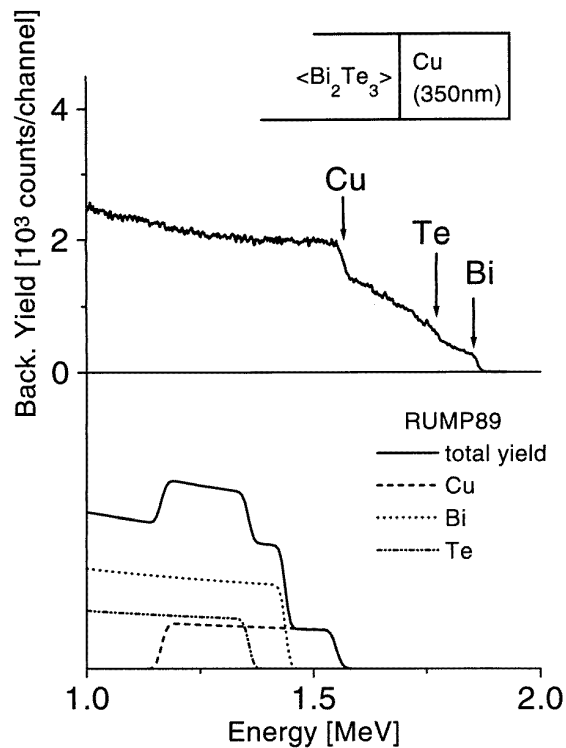
**Figure 2.** 2.0 MeV $^4$He backscattering spectrum of an as-deposited Bi$_2$Te$_3$/Cu(350 nm) sample (top), together with the RUMP89 simulation of a 350 nm Cu layer on a bismuth telluride substrate, without any interdiffusion, and the simulated individual component yields (bottom).
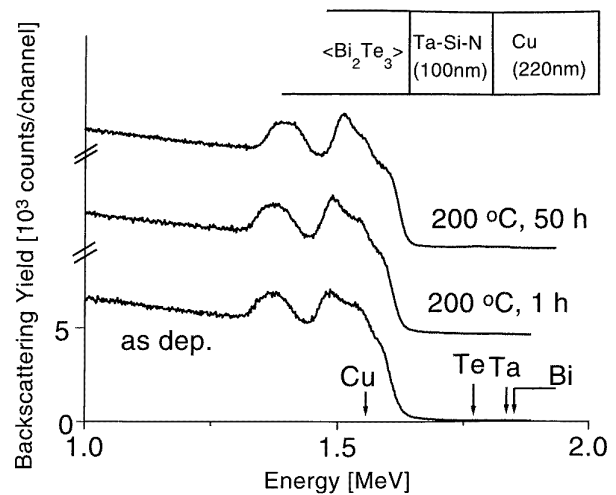


**Figure 3.** 2.0 MeV $^4$He backscattering spectra of Bi$_2$Te$_3$/Ta–Si–N(100 nm)/Cu(220 nm) samples, as deposited and annealed at 200 °C for 1 or 50 h.

backscattering yields of each single element. Arrows on the abscissa mark the energies for $^4$He particles backscattered at the surface from bismuth, tellurium, copper, platinum or tantalum. Owing both to the overlap of the various signals and of the large scattering cross sections of heavy elements, the backscattering technique is quite sensitive to out-diffusion of Bi and Te (surface concentrations of about 0.1 at% of these elements are detectable), but much less so to in-diffusion of Cu. Cu concentrations exceeding about 5 at% in the Bi$_2$Te$_3$ substrate are visible.

The crystallographic phases present after deposition and upon annealing were monitored by x-ray diffractometry with Co K$\alpha$ radiation and an Inel position-sensitive semi-ring detector. The glancing angle against the sample surface of the incident beam was 12°. The resistivity at room temperature of the Ta$_{40}$Si$_{14}$N$_{46}$ film is 350 $\mu\Omega$ cm (derived from four-point probe measurements on films deposited on SiO$_2$ substrates) and is not expected to change significantly upon vacuum annealing at 350 °C [9].

## 3. Results and discussion

### 3.1. No diffusion barrier

The top of figure 2 gives the backscattering spectrum of a magnetron-sputtered, as-deposited 350 nm thick Cu layer on Bi$_2$Te$_3$. The spectrum clearly indicates that, on direct contact, copper and Bi$_2$Te$_3$ strongly interact already

during the deposition process. A diffusion barrier is thus essential for a stable Cu contact to Bi$_2$Te$_3$. To illustrate the magnitude of that interaction, a RUMP89 simulation of the same structure without interaction is shown for comparison at the bottom of figure 2. No Te and Bi signals appear at the surface energies of these elements without interaction, whereas surface concentrations of 7 at% for bismuth and 12 at% for tellurium are observed in the as-deposited sample. The diffusion coefficient of Cu at room temperature is about $10^{-15}$ cm$^2$ s$^{-1}$ along the *a* axis and $10^{-6}$ cm$^2$ s$^{-1}$ along the *c* axis in single-crystalline bismuth telluride [13]. Because of this extremely high diffusivity, the fast reaction observed in figure 2 is quite plausible.

### 3.2. Ta$_{40}$Si$_{14}$N$_{46}$ film

In figure 3, the backscattering spectrum of an as-deposited Bi$_2$Te$_3$/Ta$_{40}$Si$_{14}$N$_{46}$(100 nm)/Cu(220 nm) sample is plotted together with the backscattering spectra of samples annealed at 200 °C for 1 and 50 h each. It can be seen that the two spectra of the annealed samples do not differ significantly from that of the as-deposited sample. There is no evidence for out-diffusion of bismuth and/or tellurium and this in spite of the high sensitivity of the backscattering technique to elements with high atomic numbers. No changes in the slope or height either of the low-energy edge of the copper signal at 1.35 MeV and of the high-energy edge of the tantalum signal at 1.60 MeV are visible. This means that, within the sensitivity limit of backscattering spectrometry, no significant metallurgical interaction between the copper and the Ta$_{40}$Si$_{14}$N$_{40}$ film occurs after deposition and after annealing for at least 50 h at 200 °C. These results are supported by x-ray diffraction measurements; no new phases are detected after either annealing duration. It can thus be concluded that the Ta–Si–N film constitutes an effective diffusion barrier between the copper overlayer and the Bi$_2$Te$_3$ substrate for at least 50 h at 200 °C in vacuum.
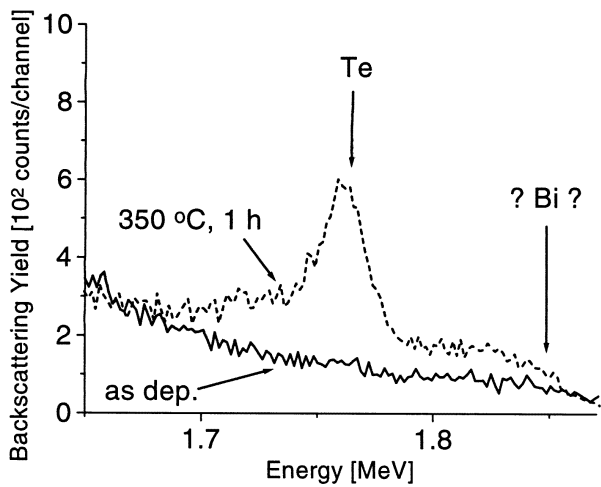
**Figure 4.** 2.0 MeV $^4$He backscattering spectra of $Bi_2Te_3$/Ta–Si–N(100 nm)/Cu(220 nm) samples, as deposited and annealed at 350 °C for 1 h, with enlargement of the 1.65–1.87 MeV energy range.
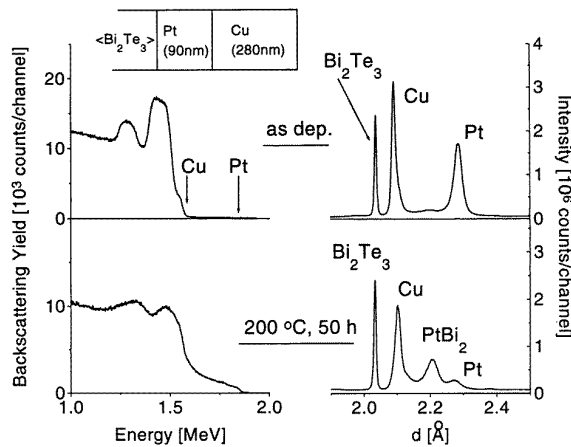


**Figure 5.** 2.0 MeV $^4$He backscattering spectra of $Bi_2Te_3$/Pt(90 nm)/Cu(280 nm) samples, as deposited and after annealing for 1 h at 200 °C and at 350 °C.

Results obtained after 1 h annealing at 350 °C were very similar; that is, no detectable interaction occurs at the $Ta_{40}Si_{14}N_{46}$/Cu interface and no new phases are detected by x-ray diffraction. However, a small peak appears in the backscattering spectrum at the surface energy of tellurium, corresponding to about nine monolayers of tellurium, together with indications of a bismuth surface contamination near the limit of the backscattering sensitivity (figure 4). One explanation is that tellurium diffuses outwards through the $Ta_{40}Si_{14}N_{40}$ layer during the annealing cycle and accumulates at the surface. A similar process would explain a surface concentration of bismuth, but with a substantially lower diffusivity than tellurium. Another interpretation is that tellurium (and bismuth) reaches the copper surface from the substrate through the vapour phase, perhaps via a selective dissociation of the bismuth telluride. The unequal amounts of Bi and Te might then perhaps reflect different sticking coefficients for adhesion to Cu. The chemical reactivities of bismuth with copper and tellurium with copper differ substantially; the system Cu–Te has stable intermetallic phases [14–16], whereas the Cu–Bi phase diagram is of the eutectic type [17]. In addition, the vapour pressure of Te is more than 1000 times that of Bi [18].

To verify or refute this vapour phase hypothesis, we annealed a $Bi_2Te_3$ sample for 1 h at 350 °C in vacuum together with a Cu foil to trap outgassing material. After this heat treatment a tellurium surface peak was present in the backscattering spectrum of the copper foil but no bismuth was detectable, which means that Bi was either not evaporated or of a surface concentration too low to be detected. We thus conclude that the tellurium peak on the copper overlayer of the $Bi_2Te_3$/$Ta_{40}Si_{14}N_{46}$/Cu sample annealed at 350 °C for 1 h most likely originated from condensation of the gaseous phase. This means that the $Ta_{40}Si_{14}N_{46}$ film is still an effective barrier for that heat treatment.
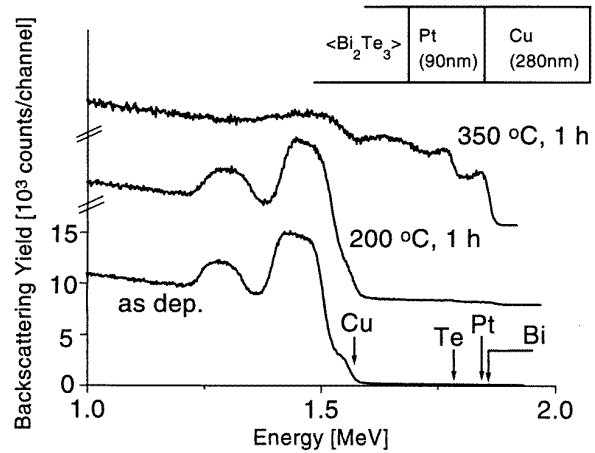
Microstructural investigation of Ta–Si–N films revealed that these films are x-ray amorphous after deposition; that is, they lack grain boundaries and short-circuit diffusion paths [9]. This result is confirmed in the present investigation, in which the Ta–Si–N is found to be x-ray amorphous after deposition. Furthermore, Ta–Si–N films are dense, with atomic densities of about $8 \times 10^{22}$ at cm$^{-3}$, and they are chemically inert with respect to copper. The diffusion of Cu into silicon is prevented up to the crystallization temperature of the diffusion barrier, which is about 900 °C [10]. Similarly low diffusivities might be expected for bismuth and tellurium on account of their large atomic sizes. Moreover, Ta–Si–N is chemically inert with respect to bismuth and tellurium in the duration–temperature regime we investigated, as we observed by x-ray diffraction measurements on the annealed samples. Inertness favours contact delamination. No such degradation was observed here or in other tests of Ta–Si–N thin-film barriers, either [5–7]. This subject deserves scrutiny.

### 3.3. Ni–7 at% V film

After a 1 h heat treatment at 200 °C, surface concentrations of Bi and Te of about 3 at% are inferred from the backscattering spectra of the annealed $Bi_2Te_3$/Ni–7 at% V(100 nm)/Cu(300 nm) sample. This means that the Ni–7 at% V film failed as an effective diffusion barrier. In contrast to Ta–Si–N, the Ni–7 at% V film is polycrystalline; that is, fast out-diffusion of Bi and Te along the grain boundaries is possible. After annealing for 1 h at 350 °C, the as-deposited $Bi_2Te_3$/Ni–7 at% V/Cu multilayer structure vanishes completely and surface concentrations of about 50 at% for Te and about 5 at% for Bi are derived by the backscattering analysis of the sample. The sample colour changes from copper yellow to metallic grey. The presence of $NiTe_2$ and $Cu_2Te$ phases is observed by x-ray diffraction after this heat treatment.

Nickel layers 3–5 $\mu$m thick are used as diffusion barrier in actual bulk thermoelectrical cooling devices [4]. Such

**Figure 6.** 2.0 MeV $^4$He backscattering and x-ray diffraction spectra of Bi$_2$Te$_3$/Pt(90 nm)/Cu(280 nm) samples, as deposited and annealed at 200 °C for 50 h. The surface energies of Cu and Pt are marked on the abscissa of the backscattering spectra of the annealed sample.

thick layers were not tested in this work, because of the need for thin stable metallizations in thick-film Bi$_2$Te$_3$ thermoelectrical devices. However, it would definitely be of interest to study the integrity of thick metal films as diffusion barriers at temperatures up to 200 °C for extended periods of time. Reviews on the reliability of Peltier coolers used as power generating modules have shown that they have a high failure rate due to contamination of Cu [19].

### 3.4. Pt film

In contrast to the Bi$_2$Te$_3$/Ni–7 at% V(100 nm)/Cu(300 nm) samples, the Bi$_2$Te$_3$/Pt(90 nm)/Cu(280 nm) samples are relatively stable after annealing at 200 °C for 1 h (figure 5). The multilayer structure remains intact, but indications of diffusion outwards of Bi and Te are revealed by the Bi and Te backscattering yields at their surface energies, corresponding to concentrations of about 2 at%. Like the Ni–7 at% V film, the Pt layer is polycrystalline. Upon annealing at 350 °C, the sample structure completely changes: large bismuth and tellurium surface intensities appear in the backscattering spectrum and their concentration ratio equals that of the bulk material. The Bi yield and, less pronouncedly, also the Te yield are somewhat peaked, which suggests a rough surface morphology. The colour of the sample changes from copper yellow to metallic grey in the process. X-ray diffractometry reveals the presence of Bi–Pt and Te–Pt intermetallic phases and of Cu$_2$Te as well. In addition to the 1 h annealing steps at 200 °C, a 50 h vacuum treatment was carried out, in order to investigate the long-time performance of the Pt film. Figure 6 shows the backscattering and x-ray diffraction results of the as-deposited and the annealed sample. The comparison of the spectra reveals that this heat treatment leads to pronounced Bi and Te concentrations at the sample surface. X-ray measurements detect the presence of Cu$_2$Te, Pt/Te and Pt/Bi intermetallic phases, whereas the Pt and Cu intensities have disappeared.

The electrical resistivity of Pt is about 35 times lower than that of Ta–Si–N, which means that a Pt layer can be 35 times thicker than that of Ta–Si–N (3.5 $\mu$m instead of 100 nm) for the same total resistance of the barrier. This resistance and the contact resistance between the various layers in the device are important factors in minimizing the total internal resistance of the thermoelectrical cooler. Although such thick layers are not desirable for fabrication of a Bi$_2$Te$_3$-based microcooler, it is clear that additional studies are required in order to determine how thin the Ta–Si–N film can be and still retain an effective diffusion barrier and also how thick a Pt layers must be to achieve sufficient thermal stability.

### 3.5. Pd film

A palladium film (110 nm thick) performs even more poorly than Ni–7 at% V and Pt. After just 1 h of annealing at 200 °C, the multilayer structure in the backscattering spectrum has completely vanished. Instead, a surface layer of Bi–Pd–Te with a stoichiometric ratio of 1:1:1 appears. A residual concentration of about 10 at% Cu was observed in this layer. After annealing at 350 °C, Cu could no longer be detected by backscattering. A surface layer of 300–400 nm thickness of pure BiPdTe (within the resolution of backscattering spectrometry) is observed. The formation of the BiPdTe phase, as well as of the Cu$_2$Te phase, was monitored via x-ray diffraction after annealing at 350 °C.

### 4. Conclusion and outlook

The Ni–7 at% V, Pd and Pt films all failed to prevent the interaction between a Cu overlayer and the Bi$_2$Te$_3$ substrate upon vacuum annealing at 200 °C for a few hours. The present results confirm the rule that pure polycrystalline metal thin films are unsuited as diffusion barriers. In contrast, the 100 nm thick Ta–Si–N film preserves the integrity of the contact for at least 50 h at 200 °C and for at least 1 h even at 350 °C. Reactively sputtered Ta–Si–N thin films appear to be good candidates for stabilizing the Bi$_2$Te$_3$/Cu system, as they have already proven for the Si/Cu system. Subjects for future experiments are the behaviour of the Bi$_2$Te$_3$/Ta–Si–N/Cu multilayer structure under frequent thermal cycling, the adhesion of the various layers, the minimum acceptable thickness of the diffusion barrier for a given heat treatment and the surface and interface morphologies. Electrical tests on thick-film Bi$_2$Te$_3$ thermoelectrical devices are required in order to establish that the contact is ohmic and that the conductivity is acceptably high. A reduction of the barrier below about 100 nm would decrease the film's resistivity and may be possible without loss of performance. Ti–Si–N films only 20 nm thick have prevented the diffusion of Cu into Si up to temperatures of 850 °C [8]. Other binary and ternary thin films like TiN, Ti–Si–N and W–Si–N may also be effective in this application and are worth investigating.

## Acknowledgments

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