

Perspective on high-entropy alloys and high-entropy nitrides as diffusion barriers for copper metallization

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Abstract: The adoption of copper as the material of choice for electrical contacts in semiconductor industry over three decades ago has been a key enabling factor for continuing the miniaturization trend that has led to faster and more efficient chips with specific functionalities. From the advanced packaging level where hybrid bonded structures are integrated in 3D with features sub-10 μm , to the front end of the line with dimensions sub-10 nm, the use of copper for signal and power transmission poses the risk of electromigration into the nearby materials, i.e. dielectric or silicon. This risk is currently mitigated by using diffusion barriers that prevent the electromigration of copper, thereby enabling significant improvements in reliability and lifetime of the contacts. Currently, the semiconductor industry uses as diffusion barrier a layer of TaN that can be about 3 nm or thicker. However, TaN is not a substrate that naturally allows for the conformal growth of copper, so surfactants (liner materials) need to be added so that metallic copper can be deposited/electroplated into vias. While the dimension and performance of the diffusion barrier is more critical for the front of the line (FEOL) metallization technologies, any materials advances for FEOL can also be leveraged to mitigate fabrication and alignment constraints faced at the back end of the line (BEOL) and the advanced packaging level. The present paper gives an account of the possible alternatives for the copper diffusion barrier, highlighting mainly high-entropy alloys (HEAs) and high-entropy nitrides (HENs). The promise of these materials as efficient barriers relies either on the absence of grain boundaries in amorphous HEAs that would act as fast diffusion avenues for copper, or on the presence of small interstitial spaces and high vacancy formation energies (in HENs) that hamper diffusion. We also mention a more drastic direction that may emerge in the future, in which copper would be replaced by other metals or intermetallic compounds: exploring such drastic choice has the potential to obviate the need for diffusion barriers altogether.

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Introduction

A current trend in the development of chip architectures is the planned spatial assembly of multiple function-specialized chips for targeted applications. Such 3D integrated technologies have been recently launched by some chip manufacturers [1, 2]; with an estimated 10^{11} transistors, 3D-integrated chiplets propel current needs in artificial intelligence, cloud computing, graphical processing units, etc. Figure 1a shows a schematic of the chip consisting in the front of the line level (FEOL, transistor level), back of the line (BEOL), and the advanced packaging level or back end. The back end and BEOL manage complex connector networks responsible for supplying the power and signal to the FEOL level. The ever-increasing transistor density at the FEOL level dictates a corresponding miniaturization and management of the metallic lines at the BEOL and back-end levels as well. The adoption of copper as the material of choice for contacts in semiconductor industry three decades ago [3] has been a key enabling factor for continuing the miniaturization trend that has led to smaller, faster, and more efficient chips. However, with the use of copper, the modern chiplet technologies faces challenges as the 3D integration technology advances. For example (Figure 1b), in order to prevent the migration of copper into silicon or the dielectric around it, a diffusion barrier made of TaN has to be present [4, 5]. Since copper cannot be conformally grown on TaN, an additional coating (liner) needs to be employed to allow the efficient electroplating of copper to fill the vias (Figure 1b). Liners presently are additional thin layers of Ta grown on TaN, although other metals or surfactants are possible [6]. The presence of liner/barrier stacks in the vias may cause problems for future hybrid bonding in heterogeneous integration and can also hamper further miniaturization. At the FEOL level, sub 10-nm wide vias may be occupied largely by the Ta/TaN liner/barrier stack and only a smaller volume fraction would be taken up by copper. As an example, an interconnect with 20 nm width $\times$ 20 nm depth with a 4 nm thick liner/barrier stack has only about 60% of its volume occupied by copper [7]. Figure 1c shows how this copper volume percentage changes as the interconnect width decreases. The smaller dimensions of copper interconnects give rise to an undesirable increase in resistivity [8], thereby affecting the power needs, cooling needs, lifetime and performance of the chiplet. A thinner liner/barrier stack (1 nm, Figure 1c) shows a marked improvement in the volume percentage of copper, but may not be effective against diffusion of Cu in the surrounding dielectric [7].

While maintaining the status-quo is a good near-term possibility, the metallization in semiconductor industry can also face different avenues going forward. One avenue is the replacement of copper as the interconnect material. Quantitative determination of the product of bulk resistivity ρ_0 and electron mean free path λ [9] shows that there are better alternatives than Cu (i.e., lower $\rho_0\lambda$), such as Rh, Ir, Ni, Ru -- with Rh being the most promising. Of these, Ni is the most abundant and economical, hence it is more likely to end up being used in large production scales. Advantages of using Ni instead of copper would

come from better thermal stability (melting point of Ni is 370 °C higher) and the smaller $\rho_0\lambda$ product (by a factor of 1.64). However, in terms of managing the interconnect lines and their interfaces with the dielectric and silicon, Ni is similar to Cu, in that Ni also has small atoms that would diffuse easily in silicon and silica [10]. Hence, choosing Ni as interconnect would require at least a diffusion barrier. Other metals, Rh, Ir, Ru, have somewhat larger atomic size and studies into the (necessity of the) barrier layers have yet to be carried out. Another direction, which has to be undertaken regardless of whether or not copper remains the metallization solution or not, more research efforts have to be devoted to the discovery of materials for high-performance diffusion barriers against the electromigration of copper or alternatives. As mentioned, the Ta/TaN stacks are widely used, while laboratory efforts are aimed at improving the liner and/or barrier performance. It appears necessary to expand the space of materials that can revolutionize diffusion barriers, and that would come from alloying; in particular, from high entropy alloying (i.e. five or more metals in alloys or cations in nitrides), where a large degree of control over composition can be exercised. While the roadmap for new metallization solutions for future technologies is complex, we focus here on the current status of barrier layers. These efforts are ongoing, and it is very likely that solutions for copper will hold for alternatives identified above (Rh, Ir, Ni, Ru) as well.

The present article focuses on specifically on highlighting the prospects of high-entropy alloys (HEAs) and high-entropy nitrides (HENs) as materials for the diffusion barrier layer for copper metallization in terms of compositions, maximum operating temperatures, and thickness ranges in which these materials can function as effective barriers against copper diffusion. Recent literature suggests that TaN may have reached its limitations [7], and novel solutions are likely to emerge from opening up the compositional space. We surmise that the richness of the composition space of amorphous and nanocrystalline metallic glasses or high-entropy nitrides (amorphous or not) can hold the key to discovering materials that possess more of the desirable properties as diffusion barriers, e.g., smaller thickness, higher thermal stability and/or increased operation temperature, tunable thermal expansion coefficient, increased adhesion to copper and silica/silicon, etc. Whether such alloys or ceramics (HEAs or HENs) make it into mainstream production at the front/back of the line or in advanced packaging, it remains to be seen, as it depends on the parameters (composition, thickness, maximum temperature) that enable reliability of the barrier function.

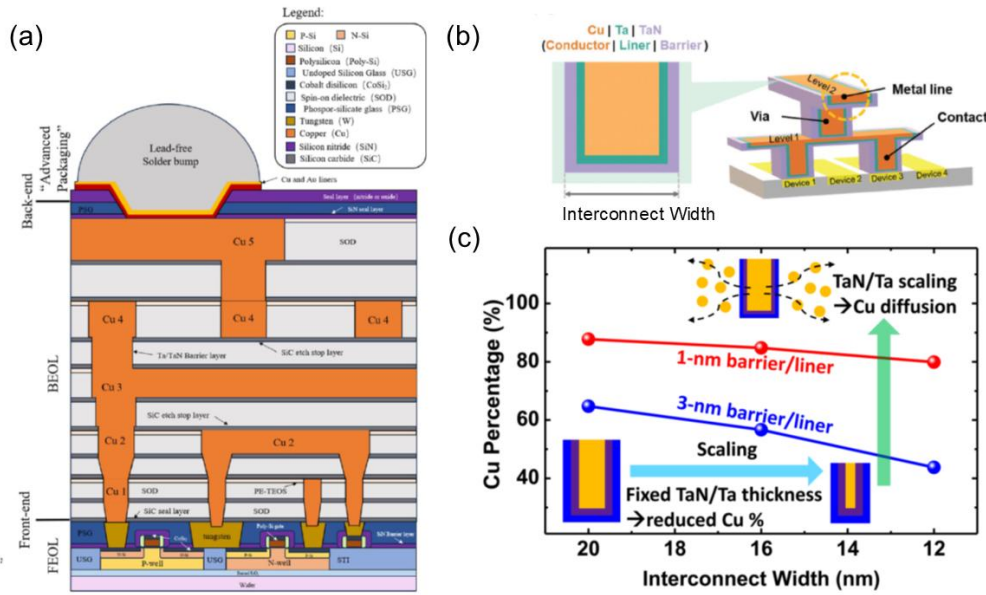


Figure 1. (a) Schematic of the front of line (FEOL), back of the line (BEOL), and advanced packaging (back end). (b) Two levels of the interconnect, with the inset showing multilayered material structures that enable copper plating on a liner/diffusion barrier stack. (c) As dimensions of the vias are reduced, the copper volume filling decreases thereby leading to increased scattering and lower conductivity. Reproduced with permission from Wiley-VCH [2] and Elsevier [7].

Current status of HEA and HEN as Diffusion Barriers

TaN can be grown as polycrystalline material on silica or silicon, and acts as a diffusion barrier [3]. Over time, its thickness for functioning as an effective copper diffusion barrier was decreased from 25 nm [4] to 5 nm or less [11]. Deposition techniques and control are responsible for this advance, with atomic layer deposition (ALD) yielding thinner and better performing TaN layers [12-14]. While vacancies and other deviations from stoichiometry can facilitate copper diffusion, it is currently believed that grain boundaries in polycrystalline TaN offer rapid diffusion pathways and have to be avoided if further advances in diffusion barrier performance are to be made [7]. Therefore, alternative materials for better performing diffusion barriers should not have grain boundaries, hence they should either be single-crystalline or amorphous; we note, however, that the former option is technologically prohibitive. While metals and metallic alloys are usually (poly)crystalline, appropriate compositions of five or more metallic species (high-entropy alloys, HEAs) can lead to bulk metallic glasses, which are thermodynamically stable as amorphous materials [15, 16]. Furthermore, there are also possibilities to create amorphous metallic materials via rapid quenching

[17] that prevents the system from finding the (supposedly thermodynamically stable) crystalline state. The usual technique for depositing HEA or HEN films is reactive magnetron sputtering [18], which allows for the deposition of films that are kinetically trapped away from the thermodynamic equilibrium. As such, this technique alone can lead to amorphous barrier materials for temperature ranges where self-diffusion is negligible and cannot lead to crystallization. Figure 2 shows the experimental characterization of two different amorphous HEAs (aHEAs), AlCrTiZrMo and TiVCrZrHf, which were tested as barrier materials between a copper layer and an oxidized layer of silicon [19, 20]. Figures 2b, d show the X-ray diffraction (XRD) patterns of the as-deposited HEA films, as well as the XRD patterns after annealing at different temperatures. The as-deposited HEAs show just a broad peak (Figure 2 b, d), which persists after annealing up to 700 °C for AlCrTiZrMo and 600 °C for TiVCrZrHf; this single broad peak is the signature of the amorphous phase. Annealing of AlCrTiZrMo HEA at 800 °C leads to the presence of Cu₃Si, indicating the interdiffusion of Cu and Si and thus the failure of HEA as diffusion barrier. In the case of TiVCrZrHf, annealing at 700 °C leads to the crystallization the amorphous HEA in the fcc phase [Figure 2(d)] as well as to the formation of copper silicide phase [20].

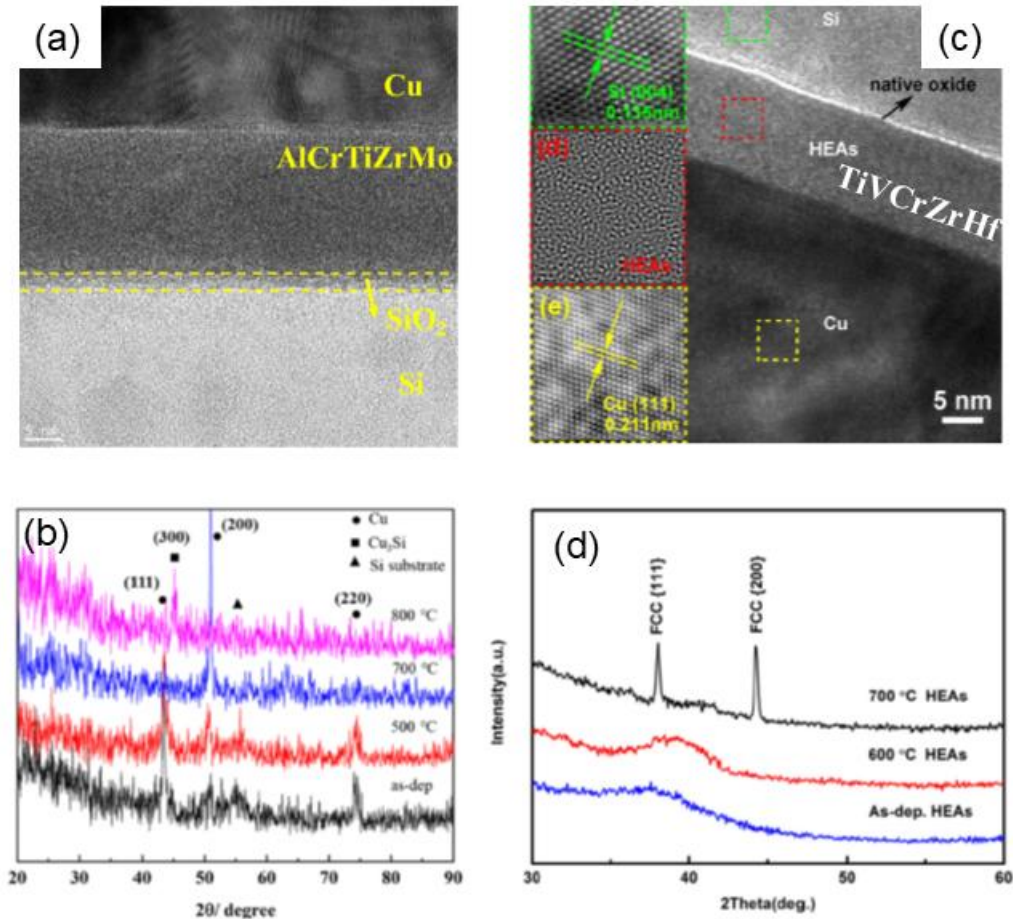


Figure 2. (a, c) TEM and (b, d) XRD characterization of HEA diffusion barriers separating copper and silicon/silicon oxide for (a, b) AlCrTiZrMo and (c, d) TiVCrZrHf. Reproduced with permission from Elsevier [19, 20].

Research over the past two decades has led to multiple reports of HEA compositions used as diffusion barriers. Table I summarizes the compositions of reported HEA copper diffusion barriers, with the corresponding thickness and the maximum temperature at which these films are still effective against copper diffusion. In terms of thicknesses, the tested range for HEA coatings is from 5 nm to 50 nm, with operating temperatures up to 800 °C. Most compositions reported in Table I are amorphous, thus fulfilling the premise that avoiding grain boundaries in polycrystalline materials is an effective way to prevent copper diffusion. Nevertheless, current research [21] also shows two examples of bcc-crystalline HEA that still prevent copper diffusion up to 650 °C; a closer inspection of the XRD patterns in the work of Gruber et al. [21] shows that these peaks are not very well-defined, suggesting that the structure may in fact be nanocrystalline, i.e., containing both amorphous and crystalline regions. Such a nanocrystalline microstructure can explain why the bcc HEAs in Table I are still effective barriers. Other interesting compositions to point out from Table I are AlCrTaTiZrRu and NbMoTaW/TiVCr where six components are present, either homogeneously [22] or in layers [23], leading to the highest operating temperature, 800 °C. This is evidence that judicious choices for HEA compositions with more than five components can be very effective in blocking Cu diffusion pathways to the point that they bring down the barrier thickness to 5 nm. It is conceivable that further research aimed at reducing the barrier thickness via increasing the number of species in HEA would lead to viable replacements for TaN.

Table I. Summary of HEA compositions tested as Cu diffusion barriers.

HEA	Structure	Thickness (nm)	Temperature (°C)	Reference
TiVCrZrHf	amorphous	10-15	600	[20]
AlCrTiZrMo	amorphous	17	700	[19]
AlCrTaTiZr	amorphous	50	700	[22]
AlCrTaTiZrRu	amorphous	5	800	[22]
FeCoBTiNb	amorphous	10	500-575	[24]
NbMoTaW/TiVCr	amorphous layers	25	800	[23]

HfMoNbTaW	amorphous	20	650	[21]
MoNbTaWZr	amorphous	20	550	[21]
MnMoNbTaW	amorphous	20	650	[21]
CrMoNbTaW	amorphous	20	700	[21]
MoNbTaVW	bcc	20	650	[21]
MoNbTaTiW	bcc	20	650	[21]

While increasing the number of species (beyond five) for HEA barriers has not been systematically pursued as a way to enhance barrier properties, the synthesis of other materials –such as complex refractory nitrides (HENs) to replace the crystalline TaN is an active area of research. There are two physical hypotheses operational for HENs as copper barriers. First, it is the avoidance of grain boundaries through the formation of amorphous or nanocrystalline structures, which is similar to the above discussion on HEA. The second operational hypothesis is the reduction of the interstitial spaces (hence increasing diffusion barriers for Cu) via formation of refractory nitrides, which generally have shorter bonds than HEAs. Relatedly, refractory nitrides generally have higher melting points than metals or alloys, which are correlated with stronger and shorter interatomic bonds (metal to nitrogen): these shorter bonds are responsible for smaller interstitial spaces, hence higher diffusion barriers may be expected. Indeed, TaN and TiN are refractory nitrides already used as barriers. Furthermore, Table II shows generally larger operation temperatures for HENs than for HEA barriers (Table I). At the same time, we note the presence of a significant number of crystalline rocksalt structures, as well as amorphous nitride structures with similar thicknesses and operating temperatures. This indicates that both avenues mentioned above (i.e., amorphization and short metal-nitrogen bonds) are at play in enabling the diffusion barrier functionality for some of the HENs listed in Table II.

Table II. Summary of HEN compositions tested as Cu diffusion barriers.

HEAN	Structure	Thickness (nm)	Temperature (°C)	Reference
(HfMoNbTaW)N	rocksalt	20	900	[25]
(MoNbTaWZr)N	rocksalt	20	900	[25]
(MnMoNbTaW)N	rocksalt	20	810	[25]

(CrMoNbTaW)N	rocksalt	20	810	[25]
(MoNbTaVW)N	rocksalt	20	810	[25]
(MoNbTaTiW)N	rocksalt	20	940	[25]
(AlCrTaTiZrMo)N	amorphous	10	800	[26]
(Al,Cr,Nb,Ta,Ti)N	amorphous	15-30	800	[27]
(AlMoNb SiTaTiVZr)N	amorphous	70	850	[28]
(AlCrTaTiZr)N	amorphous	10	900	[29]
(TiVCrZrHf)N	amorphous	10	800	[30]
(TiVCrZrHf)N _{0.4}	amorphous	10	650	[30]

The data collected in Tables I and II shows that the maximum operating temperature for HEA and HEN as barriers can be as high as 940 °C, which is 89% of the absolute melting temperature of copper. This value should serve as an upper bound for the temperatures that can be achieved during processing or operation --anything higher may lead to melting of the conductor if temperatures fluctuate. Even though operation temperatures in chips/chiplets are nowhere near 940 °C, targeting such high temperatures for barrier functionality is worth pursuing since the diffusion is more effectively suppressed at actual (lower) operating temperatures. It is instructive to take a closer look at how the barriers made of HEA or HEN can fail, and whether there are phase changes accompanying the failure. To this end, Grubber et al. [21, 25] synthesized multilayer structures consisting of Cu/HEA/Si and Cu/HEN/Si, and monitored the evolution of phases in these stacks with temperature, as well as that of their electrical resistance. Figures 3a,b summarizes this structural evolution for a subset of the compositions listed in Tables I and II. In the vicinity of the barrier failure temperatures, Figures 3a,b indicate that HEA silicides and Cu₃Si can both occur, although in certain cases [(HfMoNbTaW)N, (MoNbTaTiW)N and (MoNbTaWZr)N in Figure 3b] only the latter forms, with the diffusion barrier retaining its composition but crystallizing fully or partially. Crystallization is accompanied by the formation of grain boundaries and the ensuing enhancement in copper and silicon diffusion through the HEA barrier layer. Interestingly, the thermal effects on barrier failure are not restricted to crystallization of the amorphous barrier layer and the formation of the new copper silicide phase. For sufficiently large temperatures (950 °C), copper can also de-wet from the surface of HEA, which is likely due to the variation of interfacial energy with temperature –as Cu is still over 100 °C away from melting. Control of de-wetting at large temperatures can be exercised with appropriate surfactants that increase the binding with copper and/or via experimenting with different barrier material compositions.

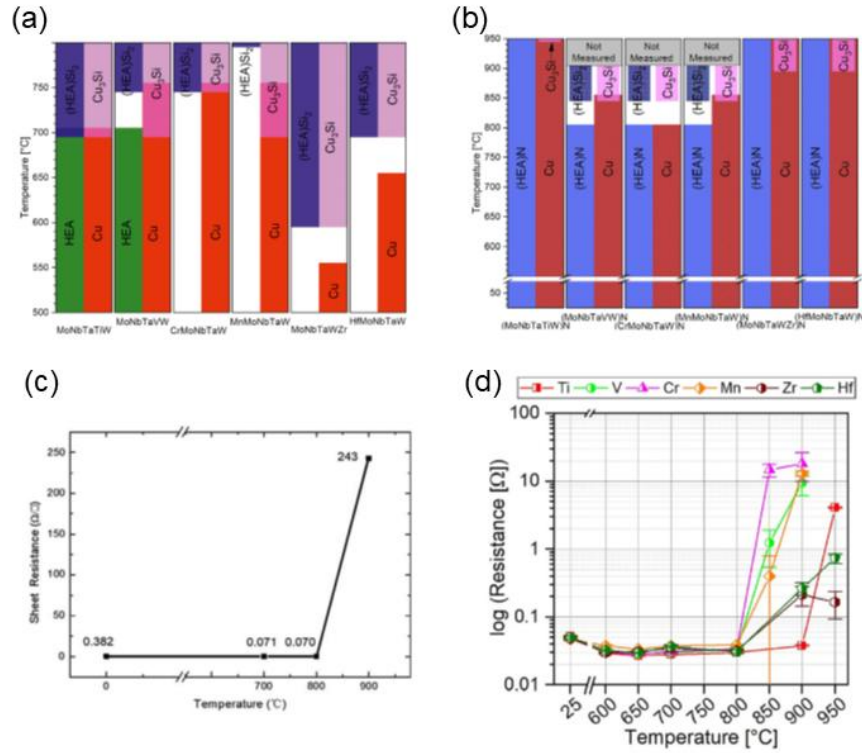


Figure 3. (a,b) Summary of the thermal evolution for (a) six HEAs and (b) six HENs used as copper diffusion barriers with the thickness summarized in Tables I and II. Annealing behavior at different temperatures was studied to probe the maximum range of temperatures before the barrier function breaks down. Diffusion barrier failure manifests through the formation of high-entropy silicides, Cu_3Si , or dewetting of copper from the barrier layers. (c,d) Evolution of electrical resistance of the diffusion barrier layer with annealing temperature for (c) a typical HEA and (d) several HENs. When not otherwise reported, some of the temperatures in Table II are taken from panel (d) of this figure as the highest temperatures below the order of magnitude jump in the electrical resistance of the barrier. Reproduced with permission from Elsevier [21, 25].

Lastly, another direct test of the diffusion barrier performance of HEA and HEN is measuring the electrical resistance of the barrier layers. Examples of electrical resistance measurements are shown in Figure 3c,d. These variations of electrical resistance are not directly associated with the diffusion of copper, since the measurements are done on isolated barrier layers. Rather, the resistance jumps shown in Figure 3c,d can be associated with the partial crystallization of HEAs or HENs and the formation of grain boundaries --which increase electron scattering, hence resistance. Assessment of failure temperature from resistance measurements is in good agreement with the temperatures at which the silicide phases begin to occur (Figure 3a,b). While most reports to date show an onset-type of behavior [7], a closer look indicates

that annealing first leads to a slight decrease in resistance with temperature (Figure 5b), which is subsequently followed by the orders of magnitude jump at the failure temperature.

Concluding Remarks

In summary, we have surveyed recent reports on using HEAs and HENs as copper diffusion barriers to possibly replace TaN in semiconductor industry. While the absence of grain boundaries in amorphous HEA leads to effective functionality as diffusion barrier, thermal treatment or prolonged operation may result in crystallization of the HEA and failure as diffusion barrier. HENs can be effective as diffusion barriers even as crystalline materials, because of the significantly smaller interstitial spaces in refractory nitrides as compared to metallic alloys. Presently, it appears that HEAs and HENs are not yet at the point of being sufficiently thin to replace the TaN barriers at the FEOL level, but they may become very competitive for BEOL and advanced packaging levels, where the need for miniaturization is not as stringent. This situation may improve with further research and experimentation, especially if computational screening approaches are employed for guiding the synthesis of HEAs and HENs. Such approaches may be used to identify domains of the compositional space where, for example, HEAs are thermodynamically stable in amorphous form, so the as-deposited films can be annealed to their stable (amorphous) structures and used as such. Forays into various regions of the compositional space, and possible expansion of this space to include more than five metallic species, may open novel avenues for enhancing the performance, functionality, and applications for HEAs and HENs in semiconductor industry. Furthermore, research on the properties of metallic contacts with small dimensions [9] shows that there may be other metals (e.g. Rh, Ir, Ni, Ru) that offer better options than copper in terms of resistivity and electron mean free path. Whether these metals require a diffusion barrier or not remains to be seen, but it is worth pointing out that if they do, then all of them are larger than copper so the HEA and HEN discussed in this review will work even better for the next generation of metallic contacts.

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