Interfacial adhesion of alumina thin films over the full compositional range of ternary fcc alloy films: A combinatorial nanoindentation study

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HIGHLIGHTS
- Thin films with large compositional gradients were made by wedge deposition with programmable shutters and post-annealing.
- 50nm AuAgPd and AlCuAu ternary fcc alloys were sputter deposited on (0001) sapphire substrates.
- Depending on the elemental composition, a solid solution (AuAgPd) or multiple phases (AlCuAu) were obtained across the wafer.
- Alloy composition influences the growth kinetics of a 400nm Al2O3 top-coating grown via atomic layer deposition (ALD).
- Nanoindentation mapping revealed the areas of optimum alloy composition for best adhesion properties of the bilayer systems.

GRAPHICAL ABSTRACT

Abstract

Combinatorial materials design of thin films allows one to investigate fundamental mechanic relationships and optimize films for engineering applications. Using a newly integrated shutter controller, specifically developed for precise control over coating design, ternary alloys with full compositional range can be deposited onto single wafers. Programmable shutters allow one to create multilayered thickness gradients of two or three different materials, which can then be annealed to create films with large compositional gradients. Two 50 nm fcc alloys (AlCuAu, AuAgPd) were magnetron sputtered onto (0001) sapphire wafers. The changing chemical composition across the wafer was investigated with energy dispersive x-ray spectroscopy and transmission electron microscopy. AlCuAu showed multiple phases and intermetallics across the wafer, whereas for AuAgPd a solid-solution was observed. Both alloys were coated with 400 nm Al2O3 (atomic layer deposition, ALD), to investigate their potential as adhesion layers for ALD coatings. Adhesion of the bilayers across the wafer was measured with instrumented nanoindentation, producing well-defined delamination-blisters. Small arrays of indents placed over the surface, each location corresponding to different adhesion layer compositions, illustrate adhesion-promoting...
1. Introduction

Thin film coatings offer a unique and powerful method of altering the surface properties of a bulk material by changing its interaction with the environment, which can then improve corrosion resistance, thermal stability or wear resistance. In every application, strong adhesion of the film to the substrate is vital for the integrity of the system and is often the main failure mechanism of the device. A common method used to help prevent coating delamination involves placing a thin adhesion layer between the film and substrate, one which adheres better to both the substrate and coating than they do to each other. Choosing the composition of this adhesion layer is rarely straightforward, since the material must interact with both the substrate and film to create a strong bond. While there are some elements known to provide good adhesion in some cases (i.e. Ti, Ta, W or Cr [1-2]), they may not be sufficient in every case, depending on the coating material and processing steps required. Therefore, it is beneficial to be able to test a wide range of alloy options and numerous compositions for each alloy to determine the optimal chemistry for the adhesion layer. This would be a daunting task if each composition has to be deposited individually, taking a considerable amount of both time and resources. Fortunately, the practice of combinatorial materials design allows for a similar investigation and optimization of material properties with significantly fewer resources and conducted in substantially less time [3-5]. In this way, alloys with a wide range of compositions can be probed on a single wafer and color, microstructure, chemical properties, and mechanical properties can be correlated to the specific composition. The time from deposition to full characterization can be reduced to a few months rather than the years it would take to conduct a similar study using traditional metallurgical methods. This method is the only logical way in which a large array of alloys can be screened for unique properties or the optimization of properties for a desired application. After an ideal composition has been identified, deposition parameters of individual targets can be adjusted or pre-alloyed targets [6] can be prepared to achieve desired stoichiometry.

To utilize this combinatorial materials design approach and create a sample with many compositions on a single wafer, a unique shutter control system has been specifically designed, manufactured and integrated into a Mantis Deposition Ltd. QPrep physical vapor deposition (PVD) system, allowing for precise control over coating design. By programming the shutters, it is possible to create these libraries either using a factorial deposition technique (similar to the ones reported in other investigations [7]) or by wedge-depositing multilayered thickness gradients of different elements. A multilayered deposition technique is used to minimize the diffusion distance so as to encourage full alloying during the annealing step, specifically for elements with high melting temperatures or low diffusion rates. With this technique post annealing is necessary to create homogeneous alloys across the thickness of the film, while limiting lateral diffusion. This innovative shutter control system has been used to create samples with a full compositional range ternary alloy, three binary alloys, and three single elements all on a single wafer. From this combinatorial material library, the properties of the alloy depending on composition can be investigated, and an ideal composition can be determined.

The current investigation tests the ability of using the high throughput combinatorial approach to develop and optimize an adhesion layer based on its chemical composition. The majority of adhesion testing methods require a large testing area, whether it is macro [8,9] or micro [10-12] bending experiments, scratch testing [13], or the simple “tape test” method [14], and thus require a specific composition over a significant area, limiting the type of sample which can be tested using any of these techniques. While these methods have been shown to produce reliable results, they also require many samples to cover a significant compositional range, making it too time intensive for a broad investigative study. For the particular combinatorial materials design approach investigated in this study, where the composition can change significantly within a short distance, there is a need for a fast method of comparing adhesion characteristics of many compositions without requiring a large test area. Therefore, the test itself must be localized to a few hundred micrometers, at most. Based on these requirements, the best method for comparative adhesion testing would be to induce delamination of the coating using nanoindentation [15]. This method is based on an energy balance relationship where the strain energy induced by the displaced indentation volume is released by the creation of new surfaces when interfacial cracking occurs between the coating and the substrate [16]. This interfacial crack is observed as a circular blister around the indent, where the diameter of the blister is directly related to the interfacial adhesion energy, with a larger blister indicating lower adhesion energy. For thin coatings these blisters can be on the order of a few tens of micrometers, indicating that this method is extremely localized and ideal for samples where the composition changes within short distances.

2. Materials and experimental methods

2.1. Synthesis and characterization of fcc films

Using a newly integrated shutter controller designed and built by a joint collaboration with Alemnis AG (Thun, Switzerland), multilayered thickness gradients of three different elements were magnetron sputter deposited for each sample and then annealed to create films with a large compositional gradient; including a near full range ternary triangle, three binary regions, and three small single element areas. The shutter control unit consists of a substrate holder stage with two sets of shutters, one set movable parallel to the x- and the other parallel to the y-axis. Single crystal silicon blades, glued onto nanometer precision linear stepper motors, define the area of exposure during sputtering and are programmed to be continuously moved during deposition. This movement produces rectangular wedges (25 × 20 mm) with a thickness gradient for each element. When changing from one element to the next, the substrate is rotated by 120° via a rotational stage. The resulting ternary triangle has an edge length of approximately 20 mm. To minimize shadowing, the shutter blades are mounted very close to the substrate, in the range of 100 μm.

Two fcc films, AlCuAu alloy and AuAgPd solid-solution alloy, were deposited onto (0001) sapphire wafers to a thickness of approximately 50 ± 5 nm. The AlCuAu alloy was deposited in such a way as to obtain the majority compositional range ternary triangle. To do this, the following cycle was repeated three times: Al wedge deposition (15 nm to 3 nm), substrate rotated 120°, Cu wedge deposition (10 nm to 2 nm), substrate rotated 120°, and Au wedge deposition (5 nm to 0 nm). The AuAgPd film was deposited in a similar manner, with each elemental wedge thickness ranging from 15 nm to 0 nm. The sputter parameters for the two different fcc alloys are summarized in Table 1. After wedge deposition, both films were annealed under vacuum at 350 °C for 2 h (ramp rate of 10 °C/min) to alloy the layers without oxidizing the surface of the film. Considering the individual elements in the ternary systems, the chosen annealing temperature was deemed high enough to encourage diffusion at the short distances of the individual wedge thicknesses. The chemical compositions were verified using
around 1% \[18\]. This would result in an error of about ±2 nm for the two following the technique used by Marshall and Evans \[15\]. The AlCuAu TMA was kept at room temperature and H₂O at 40 °C, with Ar used as thermally grown ALD determined from focused ion beam (FIB) cross-sectional imaging. For different wafer systems. The different growth rates on the two different for trimethylaluminium (TMA) and 1-2-60 s for H₂O for 3800 cycles. 220 °C with a precursor sequence of pulse-exposure-purge at 1-2-30 s from the sapphire substrate did not add to the Al composition calculation in the sample. TEM samples of selected areas on the wafers were prepared by a focused ion beam liftout process. TEM imaging was conducted on a JEOL JEM2200fs equipped with a JEOL EX-24065JGT energy-dispersive X-ray spectrometer (EDS) and a FEI Titan Themis TEM equipped with the SuperEDX system (ChemiSTEM technology) for the analysis of sample microstructure and composition. The expected error is within 5%, as relatively heavy elements and a sensitive EDS system have been used.

2.2. Atomic layer deposition (ALD)

An amorphous and stoichiometric Al₂O₃ layer was deposited by atomic layer deposition (ALD) on top of the fcc adhesion layers at 220 °C with a precursor sequence of pulse-exposure-purge at 1-2-30 s for trimethylaluminium (TMA) and 1-2-60 s for H₂O for 3800 cycles. TMA was kept at room temperature and H₂O at 40 °C, with Ar used as the carrier and purging gas. The chemical composition, density and growth per cycle at different deposition temperatures have been previously reported in \[17\]. These deposition parameters resulted in an ALD film thickness of approximately 415 nm and 380 nm for the AlCuAu and AuAgPd system, respectively. The thickness of the ALD layers was determined from focused ion beam (FIB) cross-sectional imaging. For thermally grown ALD films (≥50 nm) thickness homogeneity is typically around 1% \[18\]. This would result in an error of about ±2 nm for the two different wafer systems. The different growth rates on the two different samples are likely due to a difference in the nucleation rate of Al₂O₃ on the noble metal surfaces and are slightly lower than the growth-per-cycle on silicon substrates at this temperature reported in literature \[17\].

2.3. Adhesion testing

Arrays of load controlled indents were made using an MTS Nano Indenter XP with a 2 μm radius, 120° opening angle, conical diamond tip, following the technique used by Marshall and Evans \[15\]. The AlCuAu alloy film was indented to a load of 60 mN whereas the AuAgPd alloy could only withstand a load of 25 mN before cracking. Indentation resulted in local delamination of the coating around the indent in the form of blisters (buckles). Any indents which resulted in a cracked blister were removed from the data set. The resulting blisters were measured with Digital Holographic Microscopy (DHM) using the phase output from a single 666 nm source to measure a height profile across the blister diameter. Due to the sheer volume of indents, the most efficient way to determine the blister dimensions of hundreds of indents is to use DHM. It offers nanometer scale height resolution and a lateral resolution similar to optical microscopy, which is important for the type of blisters under investigation. Fig. 1 shows a representative DHM phase image of a blister and the corresponding extracted height profile. The diameter of the blister, 2b, was taken to be at the first minima away from the center of the blister, while the height, δ, was taken to be the highest point on the blister above the surface. Blister dimensions (diameter and height) are required for the subsequent calculation of interfacial adhesion energies. Typically, multiple blisters (total 30) are measured to statistically determine the adhesion energy of a particular coating-substrate combination. In our case, each blister corresponds to a different chemical composition. Three measurements of each indent were averaged to reduce the effect of any asymmetry in the blister. For blister diameters measured with DHM, the combined instrumental and operator error, 0.3 μm, was found to dominate over any scatter in actual blister diameters, as detailed in the paragraph below. The average scatter in the measured blister height was determined as 5 nm, where the instrumental error is only 0.3 nm according to the manufacturer. The resulting error in the calculated adhesion energy accounting for the dominant blister height and width instrumental errors and data scatters is 0.11 J/m², reported as standard deviation. Cross-sections of the blisters were created using a Tescan Lyra/XMU dual-beam FIB and imaged on a cold field emission Hitachi S–4800 high resolution scanning electron microscope (SEM).

The stochastic variation in blister diameter was determined by measuring the diameter of 9 blisters in an 80 × 80 μm area in the center of each of the Al-Au-Cu binaries. Two measurements per blister were taken orthogonally to one another, to give a sample size of 18 for each binary. The blister diameters varied by (7.1 ± 0.4), (7.3 ± 0.5), (7.3 ± 0.3) μm using 70, 60 and 30 mN loads for the Al-Cu, Al-Au and Au-Cu binaries respectively, where the errors given are the standard deviation of the measurements. Two blisters in the Au-Cu area failed or cracked, reducing the sample size to 14. A further analysis of the error of blister diameter in a single measurement was performed by repeated measurement of one orientation of a blister in the Al-Cu area. The standard deviation of 11 measurements was 0.3 μm. This is similar to the error calculated previously, suggesting the DHM noise is the main source of error rather than a random spread of blister diameters in a compositionally constant element. It is therefore an absolute error associated with all measurements performed using DHM, and is valid for the following results.

### Table 1

| Target material | Sputter current [mA] | Plasma potential [V] | Average power [W] | Deposition time [s] | Base pressure [mbar] | Process pressure [mbar] | Argon flow [sccm] |
|-----------------|----------------------|----------------------|-------------------|--------------------|----------------------|------------------------|------------------|
| Al              | 200                  | 439                  | 88                | 360                | 4 × 10⁻⁷             | 3 × 10⁻³               | 10               |
| Cu              | 150                  | 392                  | 59                | 282                | 4 × 10⁻⁷             | 3 × 10⁻³               | 10               |
| Au              | 50                   | 440                  | 22                | 170                | 4 × 10⁻⁷             | 3 × 10⁻³               | 10               |
| Ag              | 50                   | 383                  | 19                | 450                | 2 × 10⁻⁶             | 4 × 10⁻³               | 100              |
| Pd              | 200                  | 451                  | 90                | 375                | 2 × 10⁻⁶             | 4 × 10⁻³               | 100              |
| Au              | 50                   | 432                  | 22                | 270                | 2 × 10⁻⁶             | 4 × 10⁻³               | 100              |

**Fig. 1.** Local delaminations (blisters) induced via nanoindentation to measure interfacial adhesion. a) Representative DHM phase image and b) extracted height profile of a blister to determine the blister diameter, 2b, and height, δ. Statistical scatter in the data from repeated measurements is reported in the text as standard deviation but not in b), as it refers to a single measurement.
2.4. Model for indentation adhesion methodology

The indentation adhesion testing used in this investigation is based on the method used by Hutchinson and Suo [7] to calculate the interfacial fracture energy. Indentation induces an in-plane compressive stress in the film, which increases until the critical buckling energy is reached, resulting in a circular blister centered on the indentation. The minimum stress needed to generate a buckle, $\sigma_b$, is dependent on the film properties (Young's modulus, $E$, Poisson's ratio, $\nu$, thickness, $h$) and on the geometry of the blister (radius $b$). The driving stress that induces the buckle, $\sigma_b$, can be calculated if both the radius, $b$, and the height, $h$, of the blister are known.

$$\sigma_b = \frac{\mu^2 E}{12(1-\nu^2)} \left(\frac{h}{b}\right)^2$$

(1)

$$\sigma_d = \sigma_b \left[ c_1 \left(\frac{\hat{\delta}}{E}\right)^2 + 1 \right]$$

(2)

where the constant, $\mu^2$, is equal to 42.67 for a pinned blister and $c_1 = 0.2473(1 + \nu) + 0.2231(1-\nu^2)$. The blister geometry (pinned) has been identified from extracted surface profiles [19] (Fig. 1b) and FIB cross-sections [20] (Fig. 7). Together, these can be used to calculate the interfacial fracture energy, or the mixed mode strain energy release rate, $\Gamma_\Psi$: $\Gamma_\Psi$:  

$$\Gamma_\Psi = c_2 \left[ 1 - \left(\frac{\sigma_d}{\sigma_b}\right)^2 \right] \left[ \frac{1}{E} \left(1-\nu\right) h^2 \right]$$

(3)

$$c_2 = \frac{1}{1 + 0.902(1-\nu)}$$

where $\Psi$ is the phase angle of loading and can be found by [7]:

$$\Psi = \tan^{-1} \left[ \frac{\cos \omega + 0.2486(1+\nu) \frac{\hat{\delta}}{E} \sin \omega}{\sin \omega + 0.2486(1+\nu) \frac{\hat{\delta}}{E} \cos \omega} \right]$$

(4)

with $\omega = 52.1^\circ$ [7], and is only valid when the ratio of the driving stress to the buckling stress is $\approx 7.6$ [19]. Knowledge of the phase angle allows for calculation of the normal mode (Mode I) adhesion energy, $\Gamma_n$, with:

$$\Gamma_n = \frac{\Gamma_\Psi}{1 + \tan^2((1-\lambda) \cdot \Psi)}$$

(5)

with $\lambda = 0.3$, which is defining the shear mode contribution to the interfacial fracture toughness, assuming a brittle interface [7]. The Mode I adhesion energy can be considered to be close to the true work of adhesion consisting of the thermodynamic work of adhesion and the energies dissipated in the film and substrate [21]. For all calculations, only $\text{Al}_2\text{O}_3$ film properties were considered. Therefore, the $\text{Al}_2\text{O}_3$ modulus, $E$, and Poisson’s ratio, $\nu$, were assumed to be 175 GPa and 0.24, respectively [22,23]. Regarding the film thickness, $h$, the measured values of the $\text{Al}_2\text{O}_3$ layer, 380 nm and 415 nm, were used for the AuAgPd and AlCuAu system, respectively. Kriese et al. [24] developed a model for buckling of multilayer films, where a combined second moment of inertia is used to calculate the critical buckling stress of bilayers. Due to the varying elastic properties of the adhesion layers across the wafer, the simplification of only considering the top $\text{Al}_2\text{O}_3$ layer was introduced. It has been observed that delamination across the wafers happens at the metal - $\text{Al}_2\text{O}_3$ interface or the metal-substrate interface, depending on the composition of the metal bond coat. This observation of the dependence of the delaminating interface on the adhesion layer composition further complicates quantitative adhesion mapping. However, in most cases (presumably the entire AuAgPd system and low adhesion regions on the AlCuAu system) delamination between $\text{Al}_2\text{O}_3$ and the adhesion layer prevails. In these cases the simplification is completely justified and has no effect on calculated adhesion values. In cases of delamination between the substrate and the adhesion layer, the thickness error introduced by neglecting of the 50 nm adhesion layer is around 12%. As a result, the calculated adhesion energies are underestimated by 29%. As it proves impossible to cross-section every single indent in the adhesion map, the stated adhesion values should be treated as qualitative indicators for better and worse interfacial adhesion, rather than absolute quantitative numbers.

3. Results

3.1. Solid-solution compositional gradient- AuAgPd

An fcc solid-solution AuAgPd alloy was deposited using the wedge deposition technique, with each wedge thickness ranging from 15 nm to 0 nm, followed by ALD deposition of 380 nm $\text{Al}_2\text{O}_3$. A grid of 25 mN load controlled indents with $500 \times 500 \mu\text{m}$ spacing was made on the ternary area of the AuAgPd/$\text{Al}_2\text{O}_3$ bilayer sample. Fig. 2 shows the results of the interfacial adhesion energy calculation based on blister diameter and height variation, superimposed over the full ternary triangle. The following color scale is used to label the results: higher adhesion energy/good adhesion and lower adhesion energy/poor adhesion are represented by green and red respectively, ranging from 0.07 to 0.56 J/m$^2$. The empty spaces in the map are due to failed indents caused by false contact or dirt on the surface, while the black squares represent cracked blisters and only constitute approximately 20% of the area.

A closer examination of the load-displacement curves of the cracked blisters shows that the sharp jump in displacement (indicating a crack in the coating) mainly occurs quite close to the maximum load of 25 mN. This suggests that reducing the load by as little as 3 mN would significantly reduce the probability of cracking while maintaining sufficient load to induce blisters in the best adhering areas. Kleinbichler et al. [25] investigated the influence of the indentation load on the observed blister morphology in brittle thin films, ranging from intended interfacial delamination to through-thickness fracture of the film or cracking of the substrate.

Ignoring the failed indents and cracked blisters, a smooth variation in adhesion across the sample is observed, with the highest interfacial adhesion energy occurring along the low Pd concentration edge and
the poorest adhering compositions in the center. Interestingly, there is also an area in the Pd rich corner, which shows similarly high adhesion energy values. These two unique results further prove the importance of this exploratory approach to identify the best noble metal materials as adhesion promoters for Al₂O₃ films. However, the entire range of interfacial adhesion energy values only spans 0.5 J/m². The relatively low adhesion energies are attributed to an overall weak interface between Al₂O₃ and AuAgPd. For a detailed correlation between measured adhesion energies and failing interfaces, readers are referred to the discussion section of the manuscript.

Four different FIB lamellae for transmission electron microscopy investigations were prepared from the three elemental-rich corners of the ternary system as well as the poorest adhering composition in the center of the triangle. Fig. 3 shows cross-sectional EDS maps relative to their position on the wafer to investigate the extent of alloying and verify the solid-solution formation in the adhesion layer after annealing. In the three elemental-rich corner compositions, there is full alloying across the thickness of the sample with some small Pd-Ag rich areas along the interfaces in the Au-rich compositions (top corner) that have not fully alloyed at the chosen annealing conditions. Interestingly, in the center composition there is full alloying across the thickness of a few grains and a maintained layer structure across others, with Ag successfully alloying across the entire cross-section. This diffusion behavior could be due to different crystallographic orientations between the different layers that have different diffusion rates in just those grains. However, since the size of these features is only about 50 nm, they are unlikely to greatly affect the adhesion results since the blisters are approximately 10 μm in diameter.

3.2. Multi-phase alloy with intermetallics - AlCuAu

A second fcc ternary alloy adhesion layer was deposited in a similar fashion as the AuAgPd alloy, but this time looking at a system that has multiple intermetallic regions in the composition space, AlCuAu (Fig. 4a). The phase diagram of this ternary system has been previously investigated by Li et al. [26] and is also shown in Fig. 4b. The specific range for this sample, determined using energy dispersive x-ray spectroscopy (EDS) in the SEM, is outlined on top of the phase diagram, with numerous areas within the sample containing intermetallic phases, consisting of two phase regions as well as single phase intermetallics such as the β, γ, and δ phases.

After subsequent ALD deposition of the Al₂O₃ top coating, adhesion of the AlCuAu/Al₂O₃ bilayer system was also examined using the same indentation technique, but with a slightly higher indentation load of 65 mN across the sample. The increased load was necessary in order to induce indentation blisters. The indents were again spaced every 500 μm and the blisters measured with DHM. Any indents that resulted in cracking of the film are not included in the adhesion data set. The interfacial adhesion energy map of this bilayer sample is shown in Fig. 5. In general, areas with a lower Al content show better adhesion than the Al rich corner of the film on the left. Furthermore, specific ‘hotspots’ for good and poor adhesion are observed. When comparing the hotspot

![HAADF STEM images and EDS maps in the elemental-rich sections of the ternary system as well as the poor adhering section in the center show structural and chemical homogeneity across the film thickness. The expected error in chemical composition is within 5%.

Fig. 3. Cross-sectional analysis of the AuAgPd adhesion layer. HAADF STEM images and EDS maps in the elemental-rich sections of the ternary system as well as the poor adhering section in the center show structural and chemical homogeneity across the film thickness. The expected error in chemical composition is within 5%.
locations with the ternary phase diagram, it is apparent that the area of poorest adhesion (red) correlates quite well with multiple areas of AlCu intermetallics and positions near the $\beta$-phase (around $\text{Al}_0.20\text{Cu}_0.30\text{Au}_{0.50}$) and the $\epsilon$-phase (around $\text{Al}_0.65\text{Cu}_0.30\text{Au}_{0.05}$) [26]. The area showing the best adhesion (green) correlates to the area around $\text{Al}_{0.25}\text{Cu}_{0.50-0.7}\text{Au}_{0.05-0.25}$, which is not labeled as a specific phase on the ternary phase diagram.

Again, FIB lamellae for cross-sectional TEM investigations were prepared in the three elemental-rich areas and the center of the ternary triangle similar to the AuAgPd sample. The results are summarized in Fig. 6. The approximate areas from which the lamellae were taken are indicated in Fig. 6 as well as in the complete ternary map of Fig. 5 (green diamond, red triangle, blue square and black star). Near the center of the ternary triangle, approximately $\text{Au}_{0.4}\text{Al}_{0.35}\text{Cu}_{0.25}$ (Figs. 5 and 6), TEM analysis shows that the film no longer exhibits the original multilayered structure from wedge-deposition. Instead, after annealing, this composition shows large grains of two different phases, which seem to be segregated through the thickness of the film. EDS line scans (Fig. 6, below the TEM cross-section) show that an Au-rich phase is segregated to the top two-thirds of the layer, while a Cu-rich phase is segregated to the bottom of the film. While the Au rich phase contains some of all three elements, the Cu rich phase does not seem to have any traces of Au. Since the deposition order was first 15-3 nm Al, followed by 10-2 nm Cu, and then 5-0 nm Au (repeated three times), it is possible that the first Al and Cu layers reacted to form an $\text{Al}_x\text{Cu}_y$ alloy without fully alloying with the Au layer, whereas the subsequent two cycles were able to form a more complicated ternary alloy or a more uniform mixture of two different phases. This type of segregation leads to different compositions at the two different interfaces (substrate vs. ALD coating), which is difficult to quantify using this technique and could change the adhesion behavior of the system, specifically determining which interface will fail.

Similar to the center of the wafer, the Cu-rich section (top corner Fig. 6) shows a slight difference in the contrast of the Dark Field Scanning TEM (DF-STEM) at the two different interfaces, depending on the location. The EDS line scan (below the TEM image in the insert) shows uniform composition across the thickness. In the Au-rich section of the film (right corner Fig. 6), there is more consistent contrast, indicating a single, uniform phase, which is supported by the EDS scan, showing the same composition along the thickness of the cross-section. It should be pointed out here that EDS line scans are given in counts, which do not directly correspond to the chemical composition. For this reason, similar levels for the Au and Cu profile are obtained, even though the sample was taken from the Au-rich corner of the wafer (marked with a green diamond in Fig. 5). EDS counts, however, do depict chemical uniformity or inhomogeneities across the coating thickness. To obtain the chemical composition, conversion of the count data would be required. The final TEM cross-section was taken from the Al-rich section of the film (left corner Fig. 6) and shows a very different microstructure after annealing, where the majority of the layered structure is preserved. According to the phase diagram, there are large concentrations of different intermetallics in the Al-rich area of this ternary alloy, which would have a much higher melting temperature and therefore would significantly slow down the diffusion of the remaining material. In this section, the composition at the two interfaces is very different, one with a majority of Al and a small amount of Cu (substrate interface) and the other with equal counts of Au and Cu (coating interface).
Since there are actually two types of interfaces which can potentially fail, either the substrate-adhesion layer interface or the adhesion layer-coating interface, it is interesting to determine which interface is actually failing and if there is a difference across the different compositions. A change in the failing interface would explain the large spread in the adhesion energies measured on the AlCuAu wafer. To examine which interface failed during indentation, three different indents were FIB cross-sectioned along the 50 at.% Cu line of the sample, including an area with low Au content and one with low Al content. These indents also correlate to a large blister (edges) and small blister area (center). The cross-sections and their relative positions on the wafer are shown in Fig. 7. What is immediately apparent is that as the Al content increases (and Au content decreases) the failing interface changes. In the Al rich area, delamination occurs between the adhesion layer and the ALD layer. With increasing Au contents, the delaminating interface is located between the sapphire substrate and the adhesion layer.

4. Discussion

Interfacial adhesion determination using nanoindentation is a convenient and highly localized way to examine the relative adhesion energy of a film system with a changing chemical composition. However, the model for determining adhesion energy from indentation blisters [7] has a number of uncontrollable factors which hinder/complicate comparison across different film systems: dependence on local changes in film thickness, dependence on indenter geometry, inability to control which interface fails, unaccounted energy loss via elastic energy transferred into the substrate, local plastic response of the film blunting crack advancement [27], and cracking in the film/adhesion layer. Local changes in ALD (± 2 nm) and adhesion layer (± 5 nm) thickness can cause 0.3% and 9% deviation in the adhesion energies during single ALD and bilayer delamination, respectively. Initial investigations have also determined that there is a dependence on the indentation load used to induce the blister. For this reason, the relative interfacial adhesion energy of each system is determined by comparing blisters induced by the same conical indenter tip, at the same applied load, and with the same thickness of Al2O3. As different indentation loads were required on the two different adhesion layers, comparison between the systems should be treated more qualitatively. The variables that are still beyond control and can change across the wafer include cracking of the film/adhesion layer, local adhesion layer plasticity, and specifying which interface fails. With the chosen analysis approach of only considering the Al2O3 layer, the geometrical impact of metal-substrate versus metal-Al2O3 delamination is such that it underestimates the total film thickness by 12% and the calculated adhesion energy by 29% for blisters failing at the metal-substrate interface. However, as discussed in the following paragraphs, metal-Al2O3 delamination prevails in many cases, with no such related error. The influence of variations in the local elastic and plastic behavior of the adhesion layer are harder to estimated, and strongly depend on the specific material system under investigation. For homogeneous systems such as AuAgPd gradual changes are expected, while for more complex systems more sudden changes can occur. Given the small thickness portion of the adhesion layer in the total bilayer system, these effects should be smaller than the ones discussed above. In summary, the indentation induced blister method is valuable for efficient mapping of interfacial properties. In beneficial regions layer chemistry and indent geometries definitely require a closer inspection with respect to the above specified parameters.

The AuAgPd solid-solution sample shows a gradual change in blister size, with the best adhesion occurring near the Pd corner of the triangle and along the low Pd concentration edge and the poorest in the center and on the low Ag concentration side; however, this sample has a significantly lower adhesion energy than the AlCuAu sample. The majority of the TEM and EDS cross-sections showed complete alloying of the three elements into a solid solution, as was expected, except for one sample.
that showed individual grains that retained the layered structure. Since diffusion rates are dependent on crystallographic orientation, local variations in the grain orientation can explain this observation. In general, the solid solution sample shows a gradual change in adhesion energy over a small span of 0.5 J/m², which tracks directly with the composition of the adhesion layer alloy.

When the adhesion layer has a more complicated phase diagram, a wider range of adhesion energies is observed, as well as localized regions of better and worse adhesion. For the AlCuAu ternary system, the area with the best adhesion is in the Cu-rich area, whereas the Al-rich region that shows a higher concentration of intermetallics would result in lower interfacial adhesion. Conversely, the areas with highly ductile Cu would have additional plasticity that aids in crack tip blunting. However, the main reason for the big spread in adhesion energies in this system is thought to be the change in the failing interface as a function of adhesion layer composition. High Al contents result in good adhesion between the adhesion layer and the sapphire substrate, but weak bonding between the adhesion layer and the ALD coating. As a result, delamination between the adhesion layer and the ALD coating is observed during indentation with large blister dimensions and low adhesion energies. With decreasing Al and increasing Au content, the opposite trend is observed. Bonding between the adhesion layer and the ALD coating is improved, which shifts failure to interfacial delamination between the substrate and the adhesion layer, with significantly smaller blister dimensions and higher adhesion energies. One explanation for the weakening and strengthening of the different interfaces could be the segregation effects during annealing observed in the cross-sectional EDS and TEM analysis which results in cross-sectional chemical inhomogeneity of the adhesion layer in certain areas. A second explanation may be based on differences in the thermal expansion coefficients in different areas across the wafer. Regarding the individual elements forming the ternary adhesion layer, Al (\(\alpha_{\text{Al}} = 23.6 \text{ ppm/°C}\)) has the largest thermal expansion coefficient compared to Cu (\(\alpha_{\text{Cu}} = 16.5 \text{ ppm/°C}\)) and Au (\(\alpha_{\text{Au}} = 14.2 \text{ ppm/°C}\)). The thermal expansion coefficient of ALD Al2O3 is \(\alpha_{\text{ALD, O3}} = 4.2 \text{ ppm/°C}\). This may have induced larger thermal stresses at the adhesion layer-ALD interface in the Al-rich region (i.e. after cooling from the ALD deposition temperature of 220 °C), which could promote delamination between the ALD coating and the adhesion layer upon indentation. Nevertheless, a more extensive investigation is required to determine the exact cause of the local weakening of the interface, which is beyond the scope of this work. The main interest of this study was to probe the adhesion of the system as a whole, regardless of which interface fails.

Stress distribution in the adhesion layers is another important factor to discuss with respect to the observed differences in the adhesion distribution. Residual stress mapping has not been performed in the context of this work due to experimental limitation, however, it would be possible to perform sin²psi analysis with small XRD spot sizes (μm²) for a lateral resolution comparable to that of the adhesion maps (indent spacing 500 μm). Nevertheless, a few considerations about potential stress distributions can be discussed. As long as the entire system stays metallic, which is the case for the noble AuAgPd system, moderate changes in film stress across the chemical composition are expected, as homogenous gradients are present. The gradual change in blister size observed on AuAgPd supports this assumption. For a more complex system like AlCuAu with potential phase transformations during annealing as suggested by the ternary phase diagram [26], substantial stresses can develop during phase formation and cooling. The low adhesion energies observed in the potential multiphase regions of AlCuAu could partly result from those stresses.

Comparison of the adhesion energies obtained on the two different fcc layers shows that the values on AuAgPd (0.07–0.56 J/m²) are at the lower end of the AlCuAu adhesion spectrum (0.49–9.76 J/m²).
different indentation loads used for the two systems (25 mN and 65 mN) can have a small influence on the absolute adhesion values. As previously mentioned, low adhesion values in the AlCuAu system correspond to delamination between the ALD coating and the adhesion layer. Therefore, it is assumed that in the case of AuAgPd, the ALD layer delaminates from the AuAgPd adhesion layer across the entire wafer, with small changes in the adhesion energy as a function of adhesion layer composition, but no change in the failing interface. Poor nucleation of ALD layers on noble metals [30] could be a potential cause of the weak interface between Al₂O₃ (ALD) and AuAgPd.

Supporting this hypothesis, the cross-sections of the AuAgPd sample showed a thinner Al₂O₃ layer than the one observed on the AlCuAu sample, by about 35 nm. The nucleation and subsequent growth of metal oxides relies on surface reactions between the gas precursor molecules and surface OH groups. Since all of the surface elements are noble metals in AuAgPd, it is therefore more difficult to create an –OH bond on the surface to enable the nucleation of the ALD Al₂O₃ coating. After this “nucleation delay”, once there is a coalesced monolayer of Al₂O₃ at the surface, the growth proceeds in an ALD fashion on this layer. This “nucleation delay” on AuAgPd leads to a thinner Al₂O₃ layer compared to AlCuAu (380 nm vs. 415 nm) after the same number of ALD cycles (3800 cycles, 220 °C). The calculated average growth-per-cycle (GPC) is ~0.1 nm/cycle for AuAgPd and ~0.11 nm/cycle for AlCuAu. Based on the GPC value of Al₂O₃ on silicon substrates reported in literature (~0.115 nm/cycle, 220 °C) [17], the expected Al₂O₃ thickness for 3800 cycles is ~437 nm. The growth rates obtained in this study are about 5% and 15% lower, for AlCuAu and AuAgPd respectively. Groner et al. [31] report 15% lower GPC rates of Al₂O₃ on Au compared to other substrates, consistent with observed nucleation difficulties. Potentially, a more accurate representation of the growth process would be that after the “nucleation delay” period lasting for the first 200 and 500 cycles, respectively, in which the growth is slower or there is none, the growth proceeds at ~0.115 nm/cycle for the remaining cycles. A nucleation delay of hundreds of cycles has also been observed for ALD of noble metals [30]. Further studies will address the nucleation process on noble metal surfaces in more detail.

The presented methodology has a high praxis relevance. The deposition technique as well as the results can be transferred to other coating systems. The custom-built shutter system can be mounted onto various deposition chambers, replacing the standard sample holders, possibly via an adapter, thereby enabling the use of various deposition techniques. Subsequently, these systems can be used to identify alloy composition of interest. Selected chemical compositions, measured for example XRF mapping analysis, can be reproduced either from a magnetron target disc manufactured with the desired composition, or by tuning the deposition rates of the pure elements via co-deposition.

5. Conclusions

A three-component magnetron sputtering wedge-deposition method has been successfully employed to create two 50 nm fcc thin film alloys (AlCuAu and AuAgPd) with a large variation of chemical compositions on a single wafer. The intended purpose of the fcc alloys is to serve as adhesion layers for subsequently deposited ALD coatings (Al₂O₃), allowing one to study adhesion as a function of the adhesion layer composition from local delaminations obtained by instrumented nanoindentation mapping. Cross-sectional TEM and EDS analysis revealed that for fully miscible elements (AuAgPd), annealing after wedge deposition can create a uniform solid solution thin film. Uniformity is reflected in a gradual change of interfacial adhesion energies across the wafer. The relatively low adhesion values are due to a weak interface between Al₂O₃ and AuAgPd, potentially caused by a nucleation delay of the ALD process on the ternary noble metal surface. For AlCuAu, a ternary system with multiple intermetallic regions in the composition space, annealing after wedge deposition does not always create a homogeneous composition across the thickness of the layer. Segregation effects and potential intermetallic formation require complex annealing procedures to achieve through-thickness homogeneity across the entire wafer. In general, higher adhesion energy values have been observed for AlCuAu compared to the noble metal adhesion layer. Comparative indentation adhesion mapping revealed that the highest adhesion occurred in a two-phase, Cu-rich composition, with about 2× smaller indent blister diameters than in other areas on the ternary triangle. ‘Hotspots’ of low adhesion in the adhesion map correspond to intermetallic regions in the phase diagram. Furthermore, it was found that the interfacial strengths of both interfaces, the substrate-adhesion layer interface and the adhesion layer – ALD coating interface, is significantly influenced by the adhesion layer composition, resulting in a change of the delaminating interface across the wafer. High adhesion values correspond to delamination between the substrate and AlCuAu, while low adhesion energies are related to delamination between the ALD coating and the AlCuAu adhesion layer. Overall, it has been shown that a combinatorial adhesion study can be used to determine the optimum composition for improved interfacial adhesion of a particular thin film system in a holistic, yet time- and resource-saving way.

CRediT authorship contribution statement

Rachel Schoeppner: Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft, Visualization, Funding acquisition. Calum Ferguson: Investigation, Formal analysis, Writing - original draft, Visualization. Laszlo Pethő: Methodology, Investigation, Writing - original draft. Carlos Guerra-Nuñez: Investigation, Writing - original draft. Aidan A. Taylor: Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft, Visualization, Supervision, Funding acquisition. Mikhail Polyakov: Investigation, Formal analysis, Writing - original draft, Visualization. Barbara Putz: Writing - original draft, Formal analysis, Visualization, Writing - review & editing, Funding acquisition. Jean-Marc Breguet: Conceptualization, Methodology, Writing - review & editing, Funding acquisition. Ivu Utic: Writing - review & editing, Supervision. Johann Michler: Conceptualization, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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