Complex phase compositions in nanostructured coatings as evidenced by photoelectron spectroscopy: The case of Al–Si–N hard coatings

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The chemical state evolution of the Al–Si–N thin films at various Si contents is investigated by x-ray photoelectron spectroscopy (XPS). The detailed evolution of the Al 2*p*, Si 2*p*, and N 1*s* photoelectrons line positions and widths are used to identify different chemical environments as the Si content is changed. The results are compared to x-ray diffraction (XRD) data that indicate the formation of a two-phase Al_{1-x}Si_xN/SiN_y composite when the solubility limit of 6 at. % of Si in AlN is exceeded. In contrast to XRD data, no particular effect is observed in the XPS data at the solubility limit of Si. Instead, two compositional regions can be identified that are separated by a distinct change in the evolution of core level binding energy differences and chemical shifts at about 10–15 at. % of Si. This silicon concentration is identified as the onset of the formation of a SiN_y intergranular phase that is a few monolayers thick, having a chemical bonding similar to that in bulk silicon nitride. The observed changes in the XPS data coincide well with the structural changes in the material at different silicon contents. The unambiguous identification of phases, especially of minority phases from XPS data, is, however, not possible. © 2010 American Institute of Physics. [doi:10.1063/1.3460099]

I. INTRODUCTION

Nitride and carbide nanocomposite hard coatings usually consist in a complex network of crystalline and amorphous phases at the nanometer scale.^{1–5} The correct identification of all phases is crucial to understand the associated chemical and mechanical properties of these coatings. X-ray diffraction (XRD) is often used to investigate the dependence of the crystalline structure and the evolution of the grain size at different compositions.⁶ Phase identification is possible if the phases are crystalline, present in sufficient amount and with large enough grain size. However, in multiphase and multi-component systems, amorphous phases with very small volume fractions are often formed that have a major influence on the materials properties.^{3,7} Such amorphous phases, lacking long range order, remain undetectable for XRD or for any other diffraction technique such as electron diffraction in transmission electron microscopy (TEM). Moreover, the low lateral dimensions (<~1 nm) of minority phases hinder the determination of their chemical composition using for example energy dispersive x-ray spectroscopy. Techniques probing different chemical specificities are hence required to assist in phase identification. One of these techniques is x-ray photoelectron spectroscopy (XPS) that reflects atomic scale chemical interactions between atoms. It is a valuable tool to reliably identify the chemical nature of multielement nanocomposite coatings, even when minor phases are present.^{8–10} However, one element present in two distinct phases of different crystalline structure or different chemical composition may show similar chemical interactions with its environment. The identification of chemical states by XPS

does therefore not necessarily enable the unambiguous identification of phases in complex material systems.

Previously we have shown that the Al–Si–N ternary system forms an Al_{1-x}Si_xN single phase solid solution for Si contents below 6 at. %.¹¹ For Si contents exceeding 6 at. % (x=0.12) a two-phase nanocomposite forms. In the present work, we describe the chemical state evolution of the elements in Al–Si–N nanostructured films with increasing Si content by XPS. Specific issues of phase identification by XPS in nanostructured coatings, notably that of silicon nitride, are outlined by comparing XPS data with structural data obtained by XRD.

II. EXPERIMENTAL PROCEDURES

A. Deposition conditions

Al–Si–N films were deposited on silicon substrates by dc reactive unbalanced magnetron sputtering from pure Al and Si targets in an Ar/N₂ reactive atmosphere at a total pressure of 0.3 Pa. In order to detect possible influences of the growth kinetics, the coatings were prepared at two different substrate temperatures, namely, at 200 and 500 °C. The film composition was varied from pure AlN to Al–Si–N with 23 at. % of Si. This was achieved by keeping the power constant on the 5 cm diameter Al target (200 W) and varying the power applied to the silicon target of same size (from 0 up to 200 W). Pure silicon nitride (SiN_y, y~1.15 from XPS) films were also deposited. Further details about the deposition conditions and the film chemistry can be found elsewhere.^{11–13}

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B. XPS analysis

1. Analysis conditions

XPS spectra were recorded on a PHI Quantum 2000 microprobe spectrometer with a base pressure of 8×10^{-7} Pa. Monochromatic Al $K\alpha$ (1486.6 eV) radiation was used. The spectrometer energy scale was calibrated using the Au $4f_{7/2}$, Ag $3d_{5/2}$, and Cu $2p_{3/2}$ photoelectron lines at 83.96 eV, 368.21 eV, and 932.62 eV, respectively. The full width at half maximum (FWHM) of the Ag $3d_{5/2}$ line was 1.62 eV and 0.6 eV at 117.4 eV and 11.75 eV of pass energy, respectively.

The native oxide layer on top of all Al–Si–N specimens was removed by Ar⁺ sputtering cleaning at 3 kV during 90 s prior to XPS analysis. This procedure removed the typical high concentrations of oxygen (about 30 at. %) and carbon (a few atomic percent) on the surface to levels of about 4 at. % oxygen and less than 1 at. % of carbon. The oxygen content in the coatings after prolonged sputtering (not performed in the present study) amounts to 0.5–2 at. %. The sputter cleaning procedure causes a slight depletion of N in SiN_x, leading to a mean *x* value of 1.15 instead of 1.33.^{12,13} Elastic recoil detection analysis (ERDA) measurements of pure SiN_x showed that after deposition *x* is indeed 1.33, i.e., the material is accurately described as Si₃N₄. Since all samples underwent the same sputter cleaning procedure, the systematic error due to preferential sputtering of N does not alter the data interpretation presented in this paper.

Detailed spectra of the Al $2p$, Si $2p$, and N $1s$ lines were recorded after argon sputtering in steps of 0.1 eV and 11.75 eV of pass energy. The error bars (± 0.1 eV) shown in all the graphs in this work correspond to the step size of the measurements.

2. Charge correction procedure

The buildup of static charge on the surface of Al–Si–N insulating specimens following photoionization can cause significant binding energy (BE) shifts in the photoelectron lines. Simultaneous flooding with low energy electrons of 6 eV and low energy Ar ions of 10 eV was used to minimize this effect. A residual buildup of charge, however, is unavoidable but can be corrected for by the use of an appropriate charge reference.¹⁴ For charge referencing an element present in or on the specimen surface and whose chemical state is not influenced by the chemistry of the specimen can be used. A variety of charge reference procedures are commonly applied, the most common being the adventitious carbon contamination often present at the sample surface. In the present study, the native oxide layer on the coating surface was removed prior to analysis. Due to the concomitant removal of the adventitious carbon from the surface the C $1s$ line could not be used as a charge reference. In such a case the Ar $2p_{3/2}$ line of implanted argon is reported to be a reliable alternative.⁸ This technique was attempted here, but a large chemical shift (~ 1 eV) in the Ar $2p$ photoelectrons was found and attributed to matrix effects, as reported in Ref. 13. As an alternative, gold referencing was used. The gold decoration of the sputtered area of the sample was achieved as follows: the samples were fixed onto the XPS sample holder using Mo masks with a circular aperture of 1 mm in diam-

eter. Prior to XPS analysis, these Mo masks were coated with approximately 100 nm of gold. During argon sputtering of a 2×2 mm² region centered on the aperture of the Mo mask, gold atoms were sputtered from that mask, and a few of them were redeposited onto the sample surface. This submonolayer coverage was used for BE calibration purposes. The Au $4f$ line was recorded in steps of 0.1 and 11.75 eV of pass energy. In contrast to implanted Ar atoms, Au atoms were found to be not affected by changes in the chemistry and in the microstructure of Al–Si–N films. The Au $4f_{7/2}$ line position was hence used as a charge reference. By comparison to tabulated data for pure AlN and pure Si₃N₄ films, however, a shift in the Au $4f_{7/2}$ line of the order of +1.2 eV away from the line position in bulk gold (84.0 eV) was evidenced.¹³ The Au $4f_{7/2}$ reference line position was therefore fixed at 85.2 eV in the present study. This major shift in the Au $4f_{7/2}$ line was attributed to the submonolayer surface coverage and to the formation of gold islands or clusters on the sample surface, based on previous works.^{15–17} The influence of the electron and ion neutralizer on the resulting shape of the photoelectron peaks was not investigated in the present study. Using a conductive mask placed on the sample, thereby reducing the illumination and charge compensation zone on the sample prevented a differential charge buildup between illuminated and nonilluminated zones. Moreover, it was observed that the Au $4f_{7/2}$ photoelectron peaks showed a constant width over the whole concentration range of Si investigated in this work. This supports the assumption that the sample surface had a uniform charge distribution, irrespective of the composition, showing no signs of charge inhomogeneities.

3. XPS data processing

The elemental composition was determined using the MULTIPAK software package from Physical Electronics that uses proprietary relative sensitivity factors to calculate element concentrations in atomic percentages. All other data processing was performed using the CASAXPS software package. Photoelectron line shapes were fitted by Gaussian/Lorentzian products after the background was removed by an iterative Shirley procedure. Energy regions of ± 4 eV around the photoelectron peak maxima were considered for the data processing. For Al–Si–N composite films, the peak shape of the Al $2p$ and N $1s$ photoelectron lines found in pure AlN and of the Si $2p$ photoelectron line in pure SiN_y were used.¹² Although this procedure accounts only for the shape found in the binary materials, no noteworthy deviations were found in the ternary materials for Al $2p$ and Si $2p$ signals. The positions and width of Al $2p$ and Si $2p$ peaks reported in this paper refer hence to the maxima and FWHM of the fitted curves. A fit with a single symmetric line was, however, not possible for the N $1s$ signal. The N $1s$ peak was found to be slightly asymmetric with increasing Si content in Al–Si–N films. However, a fit with two Gaussian/Lorentzian lines remained unsuccessful, as mentioned in Sec. III C. The N $1s$ peak position reported in this paper was, therefore, taken as the peak maximum of the raw data; the N $1s$ FWHM was also taken from raw (unfitted) data.

FIG. 1. Evolution of the BE differences between the N 1s, Al 2p, and Si 2p photoelectron peaks as a function of the silicon content. Multiple data points for a given composition and deposition temperature correspond to fully independent XPS measurements on a given sample (new region on the sample, new mounting, etc.). Top insert: evolution of the c lattice parameter as a function of the Si content, as deduced from XRD data.

III. RESULTS

A. Evolution of BE separations

Charge referencing always suffer from uncertainties.¹⁴ As discussed above, incomplete charge compensation will cause shifts in the XPS line positions. This shift is the same for all the photoelectron peaks recorded during one measurement run on a given sample, but depends on multiple parameters in a nonpredictable fashion from one sample to another. This poses a severe impediment on measuring campaigns where a series of samples with different preparation conditions are to be compared. A way around the problem is to investigate the energy separation of two photoelectron lines of two distinct elements recorded on the same sample during the same measurement run, since charging effects will cancel out.

BE separations, ΔBE , between the main core level photoelectron lines of the three constituting elements Al, N and Si are shown in Fig. 1 as a function of the Si content. Note that, although three BE differences are presented, the absolute BEs cannot be determined, because only two of the ΔBE s are independent. In Fig. 1(a), the BE difference between N 1s and Al 2p, $\Delta BE(N\ 1s-Al\ 2p)$, is constant and

equals 323.2 eV over the whole composition range. This corresponds to the average value reported for pure AlN in literature (average value reported in Refs. 12 and 13, as determined from Refs. 8 and 18–22). In contrast, the BE difference between N 1s and Si 2p, $\Delta BE(N\ 1s-Si\ 2p)$, shifts by 0.6 eV from 295.3 eV in Al–Si–N with 1.5 at. % of Si to 295.8 eV in Al–Si–N with about 15 at. % of Si and 295.9 eV in pure SiN_y [Fig. 1(b)]. Between Al–Si–N with 15 at. % of Si and pure SiN_y, $\Delta BE(N\ 1s-Si\ 2p)$ remains essentially constant and corresponds to the average value reported for Si₃N₄ in literature (Refs. 12 and 13, as determined from Refs. 8, 18, 20, and 23). The same shift of 0.6 eV is observed for $\Delta BE(Al\ 2p-Si\ 2p)$ [Fig. 1(c)]. At 1.5 at. % and at 15 at. % of Si, $\Delta BE(Al\ 2p-Si\ 2p)$ values of 27.9 eV and 27.3 eV were found, respectively. Again the BE difference remains constant at 27.3 eV beyond 15 at. % of Si. The values reported in this work are in agreement with data previously reported for Al–Si–N, namely, 27.5 eV at 11 at. % of Si (Ref. 19) and 27.2 eV at about 25 at. % of Si.²⁴

The inset at the top of Fig. 1 shows the structural evolution of the Al–Si–N system based on our XRD data acquired previously:¹¹ the formation of an Al_{1-x}Si_xN solid solution below 6 at. % of Si and of a two-phase Al_{0.44}Si_{0.06}N_{0.50}/SiN_y composite above 6 at. % of Si is strongly supported by the evolution of the c lattice parameter in wurtzite Al(–Si)–N. The latter decreases as predicted by Vegard's law for the substitutional incorporation of Si on Al sites in AlN up to 6 at. % of Si. It remains constant for Si contents larger than 6 at. %, showing that excess Si atoms are no longer incorporated in the AlN lattice and are therefore segregated at the boundaries of Al–Si–N grains, forming there a SiN_y layer.

In contrast to the abrupt change that can be seen in the XRD data (inset), no change in the chemical evolution of Al–Si–N films is observed at 6 at. % of Si in Fig. 1. Instead, two compositions regions with distinct chemical states, a first one ranging from 0 to 15 at. % Si and a second one above 15 at. % Si can be distinguished from the evolution of BE separations. The behavior of ΔBE s shown in Fig. 1 suggests that the Al–N bonding remains unaffected by the incorporation of Si in hexagonal AlN (h-AlN), while the core electrons of silicon encounter a clear chemical shift, seemingly toward lower BEs, as the Si content is increased. Above 15 at. % of Si, all the ΔBE values remain constant: This suggests that there is no more change in the chemical environment of atoms in Al–Si–N films. In summary, the dependence of ΔBE on the Si content gives information on the evolution of the chemical state of the constituent elements in Al–Si–N composite materials. Detailed information on the chemical state, however, requires the determination of absolute BEs.

B. Charge referenced photoelectron line positions

The evolution of Au referenced BE positions of the Al 2p, Si 2p, and N 1s photoelectron peaks as a function of the Si content is shown in Fig. 2. The precision of the absolute BE determined by Au charge referencing is discussed elsewhere.¹³ Small but significant chemical shifts of less than 0.6 eV are clearly seen in Fig. 2 for all three elements. With

FIG. 2. BE evolution of Al $2p$, Si $2p$, and N $1s$ photoelectrons as a function of the Si content in Al-Si-N. The charge referencing is based on the Au $4f_{7/2}$ photoelectron line set at 85.2 eV. Solids lines are added as a guide to the eye.

increasing silicon content, the BE of Al $2p$ photoelectrons steadily increases by 0.3 eV up to the highest Si content in Al-Si-N films explored in this study, namely, 23 at. % [Fig. 2(a)]. The BE position of the N $1s$ peak shows a similar evolution [Fig. 2(c)]: it is first constant and increases then by 0.5 eV between about 10–15 at. % of Si and pure silicon nitride. In contrast, the BE position of the Si $2p$ peak drops by about 0.4 eV between 1.5 and 13 at. % of Si before it increases by about 0.3 eV up to the position reported for pure silicon nitride. As presumed from Fig. 1, the Si $2p$ line indeed shifts toward lower BEs at low Si contents. Furthermore all three recorded photoelectron lines clearly show chemical shifts, which could not be deduced from the Δ BE data.

The above described chemical shifts can be understood in terms of a simple model that considers partial charges on the Al, Si, and N atoms. From the Pauling electronegativity of Al (1.61), Si (1.90), and N (3.04) atoms, we conclude that the Al-N and Si-N bonds are of mixed ionic and covalent nature, i.e., polarized, and that the Al-N bonds in AlN are more polarized than Si-N bonds in silicon nitride. The negative partial charge on nitrogen atoms is therefore smaller in SiN_y than in AlN. This causes the kinetic energy of ejected N $1s$ photoelectrons from SiN_y to be smaller than in AlN. The BE of N $1s$ photoelectron is therefore higher in SiN_y

than in AlN, as observed in Fig. 2. In the Al-Si-N ternary system, the BE of Al photoelectrons is influenced by the increasing Si-content in the h-AlN lattice and the subsequent decrease in the Al concentration. The presence of Si atoms tends to increase the ionic character of the Al-N bonds, because it is easier for N atoms to complete their outer electron shell by attracting electrons from Al than from Si atoms. The positive partial charge on Al atoms therefore increases, lowering the kinetic energy of Al photoelectrons, i.e., increasing their BE with increasing the Si content in Al-Si-N films. Similarly, a Si atom bonded to nitrogen and surrounded by Al-N bonds is expected to be less positively charged than if surrounded by only Si-N bonds, i.e., the Si-N bond becomes more polarized going from Al-Si-N to pure SiN_y. Through this mechanism the BE of Si $2p$ is also expected to increase at higher Si content in Al-Si-N.

Such a simple charge distribution model based on Pauling electronegativities, neglecting other contributions to the photoelectron BE such as changes in the Madelung potential and relaxation effects,²⁵ may explain the chemical shifts toward higher BEs of the Al $2p$, Si $2p$, and N $1s$ peaks above 13 at. % of Si in Fig. 2. However, this simplified model fails to explain the decrease in the Si $2p$ BE and the essentially constant values of the Al $2p$ and N $1s$ BEs between 0 and 13 at. % of Si. Obviously another contribution to the BE must play a significant role in the low silicon concentration regime. Here, the formation of charge compensation defects in the Al-Si-N crystalline structure may play a significant role. Such defects form as a consequence of the extra valence electron introduced per Si atom substituting an Al atom in the Al-Si-N solid solution for Si contents below about 6 at. %. This additional electron and the concomitant defects introduced greatly influence the charge distribution in the Al-Si-N lattice and may explain that Si atoms encounter large chemical effects at Si concentrations below 6 at. %. Recent discrete Fourier transform calculations of the lattice parameters in substitutional Al-Si-N solid solutions show that the excess electrons can be localized, e.g., at Al vacancies and DX centers.²⁶

The absence of a significant change in the evolution of BE positions at 6 at. % of Si (solubility limit for Si in Al_{1-x}Si_xN) in Fig. 2 for all elements is surprising. This issue will be addressed in the discussion section below. In summary, the evolution of the BEs shows two distinct composition regions, a first one for low and a second one for high Si concentrations, with a transition around 10–15 at. % of Si, as in Fig. 1.

C. Evolution of the photoelectron line widths

Because the information obtained from the line positions as well as their BE differences seemingly does not provide a clear picture of the material's chemical states, core level line widths were analyzed in addition. The width of a given photoelectron line is related to the core-hole lifetime of the photoionized atom which depends on the chemical environment of this atom. The FWHM of a photoelectron line is, therefore, a valuable indicator of the chemical state(s) of an element. It is particularly useful if coexistent chemical states

FIG. 3. Evolution of the FWHM of Al $2p$, Si $2p$, and N $1s$ core level photoelectron lines as a function of the composition of Al-Si-N films. Solid lines are added as a guide to the eye. Dotted lines correspond to the criterion of critical line broadening indicating the existence of several chemical states of an element in Al-Si-N composite films when the FWHM of a photoelectron line exceeds $1.15\times$ the FWHM of the same photoelectron line taken in a reference material, here AlN and/or SiN_y .

cannot be detected, i.e., by the presence of a shoulder or an asymmetry of the photoelectron line. Wide band gap semiconductors such as AlN should have symmetrical photoelectron lines due to the vanishingly small density of states at the valence band. It is commonly agreed that if the FWHM ratio of a given photoelectron peak (e.g., measured in Al-Si-N films) to a reference line (e.g., measured in pure AlN or SiN_y) equals 1.15 or more, then two lines corresponding to two distinct chemical states can be assigned to fit the XPS signal. Intermediate cases of line broadening may be caused by local variations in the atomic arrangement, resulting in a distribution of local potentials which is called a “disorder broadening.”^{27,28}

In the present work, no shoulder or significant line asymmetry was observed in the Al $2p$, Si $2p$, and N $1s$ photoelectron lines. The FWHM of these lines are reported in Fig. 3, together with the critical FWHM values that correspond to the “1.15 criterion” introduced above. As shown in Fig. 3(a), the FWHM of the Al $2p$ line is constant (~ 1.6 eV) over the whole composition range. In contrast, both the Si $2p$ [Fig. 3(b)] and the N $1s$ [Fig. 3(c)] lines show a line broadening

with increasing Si content. For the Si $2p$ line in the range 1 to 5 at. % Si, large variations in the FWHM obtained from independent measurements on given samples are observed. They result from the low intensity and consequently the weak peak-to-noise ratio of the Si $2p$ photoelectron line at small Si concentrations, causing large uncertainties in the determination of the FWHM. Nevertheless it can be seen that below 10 at. % Si, the Si $2p$ line width reaches about 1.95 eV, which is just at the previously defined detection limit for two distinct chemical states [defined as 1.15 times the line width (1.7 eV) in pure SiN_y]. The broadening of the Si $2p$ line can therefore not be unambiguously attributed to the existence of distinct chemical states or to a disordered chemical state. Both effects may explain the experimental observations. Beyond 10 at. % of Si, the Si $2p$ line width progressively decreases to about 1.75 eV at 23 at. % of Si, close to the value found in pure SiN_y . At high Si contents (>20 at. %), the majority of Si atoms thus exist in a chemical state similar to that in bulk silicon nitride. The FWHM of Si $2p$ remains unchanged upon further increase in the Si content up to the highest Si concentration considered in this study, 23 at. %. The N $1s$ line width [Fig. 3(c)] increases from 1.4 eV in pure AlN to about 1.7 eV in Al-Si-N at 10 at. % Si, clearly surpassing 1.15 times the reference line widths taken in AlN (1.4 eV) and SiN_y (1.3 eV). Below about 5 at. % of Si and similar to the case of the Si $2p$ line, the broadening of the N $1s$ line is small and cannot be attributed conclusively to distinct chemical states or to a disorder broadening. Above 10 at. %, however, the N $1s$ peak can be interpreted to arise from the overlap of several lines corresponding to distinct chemical states, possibly corresponding to distinct phases. This interpretation is further supported by the small asymmetry observed on the low BE side of the N $1s$ line above 4 at. % of Si (Fig. 4). Attempts to fit this peak with a base set of two lines, the line shapes of which were chosen as best fits of the N $1s$ line in AlN and SiN_y , remained, however, unsuccessful: the relative areas under the fitted component lines could not be correlated with the amount of Si in Al-Si-N. This is attributed to a complex evolution of the chemical environment of nitrogen atoms in Al-Si-N films whose chemical states differ from those found in the binary nitrides, e.g., due to disorder broadening (see below).

Based on our prior knowledge that a phase separation into an $\text{Al}_{1-x}\text{Si}_x\text{N}$ solid solution and SiN_y occurs above the solubility limit identified at 6 at. % of Si by XRD,¹¹ the following evolution of the photoelectron line widths is deduced.

- The chemical state of Al atoms remains essentially unchanged because Al is bonded to four nitrogen atoms in all Al-Si-N films, just as in pure AlN. Al atoms are moreover little influenced by the incorporation of Si atoms in the AlN lattice because Si atoms are their second nearest neighbors only and are only present in small amounts. For a Si content above 6 at. %, the additional Si atoms form a SiN_y grain boundary phase. The chemical environment of the Al atoms contained

FIG. 4. N 1s line fitting in Al-Si-N films containing (a) 2.5 at. % and (b) 15 at. % of Si. The CASAXPS software package and a Gaussian/Lorentzian product of type GL(80) were used to fit the N 1s line. An asymmetry on the low BE tail of the N 1s line is clearly seen in (b).

in the $\text{Al}_{1-x}\text{Si}_x\text{N}$ crystallites is thus not further affected.

- N atoms have a fourfold (tetrahedral) coordination to Al atoms in wurtzite AlN and a threefold (planar trigonal) coordination to Si atoms in Si_3N_4 . A phase separation into $\text{Al}_{1-x}\text{Si}_x\text{N}$ and SiN_y necessarily leads to the coexistence of two distinct chemical states for nitrogen atoms. Hence, the line broadening above 5 at. % of Si in Fig. 3(c), by far exceeding the “1.15 criterion,” indicates the presence of at least two distinct chemical states. Each nitrogen atom in the Al-Si-N solid solution phase is bonded either to four Al atoms, or to both Al and Si atoms; this leads to a disorder broadening of the N 1s photoelectron line below about 5 at. % of Si. Moreover, the formation of charge compensation defects in the wurtzite $\text{Al}_{1-x}\text{Si}_x\text{N}$ crystalline phase (e.g., DX centers and Al vacancies)²⁶ may also lead to local lattice deformations (e.g., broken Si-N bond) which adds to the disorder broadening of the N 1s line. The latter may explain that the N 1s line could not be fitted by an overlap of the N 1s lines for pure AlN and SiN_y .
- Silicon atoms are fourfold bonded to nitrogen atoms both in $\text{Al}_{1-x}\text{Si}_x\text{N}$ and in SiN_y , except in the case of a defect-induced broken Si-N bond mentioned above. Si atoms are therefore found in a chemical state similar to that found in pure silicon nitride (i.e., no major broadening of the Si 2p line). Nevertheless, local geometrical distortions associated to the incorporation of Si atoms in the AlN lattice and to the subsequent formation of charge compensation defects may lead to some disorder broadening of the Si 2p photoelectron line as

observed in Fig. 3(b) for Si contents lower than the solubility limit of 6 at. %. For Si contents larger than about 15 at. %, the majority of Si atoms in Al-Si-N films are contained in the SiN_y grain boundary layer. Hence, the Si 2p line widths become similar to that measured in pure silicon nitride. In the composition range between 6 and 10–15 at. % Si, the thin SiN_y grain boundary layer that forms and progressively covers the entire surface of $\text{Al}_{1-x}\text{Si}_x\text{N}$ crystallites may lead to a local environment that is considerably influenced by the majority phase. The Si 2p photoelectron line is then expected to remain broadened and shifted as observed.

IV. DISCUSSION

A. Identification of a separate silicon nitride phase in Al-Si-N films

Our XPS study reveals clear chemical changes with varying the composition of Al-Si-N films, related to the complex phase composition of this ternary system. However, the data does not conclusively reflect the formation of a silicon nitride grain boundary phase for Si contents larger than 6 at. % that is conclusively deduced from XRD data.¹¹ The BE difference between the Al 2p and the N 1s peaks, $\Delta\text{BE}(\text{N } 1s - \text{Al } 2p)$, and the Al 2p line width remain constant over the whole composition range explored here [Figs. 1(a) and 3(a)]. This suggests that the chemical environment of Al atoms remains essentially unaffected by the Si-content in the Al-Si-N films. In contrast, both $\Delta\text{BE}(\text{N } 1s - \text{Si } 2p)$ and $\Delta\text{BE}(\text{Si } 2p - \text{Al } 2p)$ depend strongly on the Si content [Figs. 1(b) and 1(c)], which is related to a Si 2p line shift toward lower BEs with increasing Si content from 0 to about 13 at. % [Fig. 2(b)]. The Si 2p and the N 1s line widths also increase up to and beyond 1.15 times the reference line widths taken from the binary nitrides, respectively [Figs. 3(b) and 3(c)]. This suggests changes in the chemical environment of silicon and nitrogen atoms. We concluded that the Si-N bonds, but not the Al-N bonds are affected by the film composition. Furthermore, the distinct chemical states for nitrogen atoms observed above 10 at. % of Si in Al-Si-N films [Figs. 3(c) and 4] strongly suggests the formation of a distinct second phase, i.e., a SiN_y phase. This is further supported by the evolution of the Si 2p line width at high Si contents [Fig. 3(b)]. However, a clear distinction between Si incorporated in the Al-Si-N grains and Si located in the grain boundary phase is not possible. Thus, an unambiguous determination of distinct phases in Al-Si-N films is not possible from XPS data. Notably, the abrupt structural change at 6 at. % of Si observed by XRD (inset Fig. 1), does not lead to a correspondingly sharp change in the chemical evolution. Instead the evolution observed in Figs. 1–3 can be divided into two compositional regions below and above a Si content range of 10–15 at. %. Between 6 and 10–15 at. % of Si, the local environment of the growing SiN_y grain boundary layer is dominated by the majority phase (nanocrystalline $\text{Al}_{1-x}\text{Si}_x\text{N}$), so that the chemical state of Si and N atoms differs from that in bulk silicon nitride. The “critical” concentration of 10–15 at. % of Si is therefore attributed to the

formation of a “thick” SiN_y interlayer (exceeding 1–2 monolayers),¹² thick enough to show chemical properties similar to that of bulk silicon nitride. Despite the strong indications for a phase separation found for Si contents larger than 10–15 at. % of Si, the presence of a SiN_y minority phase in the composition range from 6 to 10–15 at. % of Si cannot be unambiguously identified in Al–Si–N films.

B. Phase identification by XPS in nanocomposite hard coatings

The identification of different phases by XPS in a complex multiple-element sample requires the correct identification of chemical states in this sample. This is commonly achieved by comparing BEs measured in given sample to literature and tabulated data for elemental materials or binary compounds. Such a comparison between data obtained in different laboratories and on different XPS apparatus requires that the chemical states to be identified are well separated by at least 1 eV, so as to take into account uncertainties inherent to charge referencing techniques. Examples are the N 1s line in Ti–Al–V–Si–N and Zr–Si–N, where Ti–N and Si–N contributions, as well as Zr–N and Si–N contributions can be resolved, whereas this is not possible for Al–N and Ti–N contributions.⁹ Similarly, the N 1s peak in Al–Cr–V–N composites studied by Franz *et al.*²⁹ could only be decomposed into N–V and N–(Al, Cr) contributions. A way to reduce the minimum BE separation required for the identification of distinct chemical states is to include the measurement of reference samples in the study of multielement films. Hence, uncertainties related to different measurement conditions and charge referencing techniques are eliminated. This also enables the study of line broadening effects, as reported in the present work, which gives further indications on the presence of distinct chemical states.

The mere identification of chemical states (e.g., Al–N, Si–N bonding states) does not prove that they are present in separate phases (e.g., AlN, SiN_y) or in one phase as a solid solution (e.g., $\text{Al}_{1-x}\text{Si}_x\text{N}$). This is well illustrated in this work by the fact that the Si 2p BE in the Al–Si–N solid solution at the solubility limit (6 at. % of Si) and in pure SiN_y are equal [Fig. 2(b)]. In this case, the detailed study of BE shifts and line broadening effects can give further indications about changes in the local environment of atoms. However, the local environment of atoms in a minority phase such as SiN_y in the Al–Si–N system is considerably influenced by the majority phase ($\text{Al}_{1-x}\text{Si}_x\text{N}$ grains). Hence, the chemical state of silicon atoms cannot unambiguously be attributed to the existence of a SiN_y separate phase by comparison to a SiN_y bulk reference. In some cases, however, such as for the widely studied silicon-containing transition metal (TM) nitride systems, additional arguments can be brought to solve this issue. Due to the high stability of sp^3 hybridized silicon, Si atoms incorporated as a solid solution in fcc TM nitrides can be expected to sit on interstitial tetrahedral sites in the lattice, forming Si–TM silicide bonds, rather than on the metal (e.g., Ti) octahedral site, that would allow for Si–N bonds. Such a silicide state may be easily distinguished from the Si–N bonding state (as well as from elemental Si) under the Si 2p peak, at least in the Ti–Si–N system. The absence

of a silicide contribution in XPS measurements is therefore usually presented as an evidence of the existence of a complete phase separation.^{9,10,30} However, a possible incorporation of Si atoms on TM sites is mentioned in the literature [e.g., for Ti–Si–N,^{31,32} Nb–Si–N,³³ and Zr–Si–N (Ref. 34)]. The formation of a $\text{TM}_{1-x}\text{Si}_x\text{N}$ metastable phase could be the consequence of low surface diffusivity due to low deposition temperature ($<500^\circ\text{C}$) and reduced energy delivered to the growing film (e.g., by ion bombardment).³² In such a case, Si–N bonds would be formed within the TM nitride phase, and neither XPS nor Fourier transform infrared spectroscopy (FTIR)³⁴ nor x-ray absorption near-edge structure (XANES)³⁵ may distinguish between a solid solution and phase segregation, similar then to the Al–Si–N case. Direct observations of several phases by XRD and TEM, as well as the observation of microstructural changes accompanying the formation of a solid solution and/or a phase separation—such as the evolution of bond length and grain size (from XRD) or the evolution of optical and electrical properties^{12,33,34}—are then required to evidence the existence of more than one phase.

V. CONCLUSION

The XPS analysis of Al–Si–N films with increasing Si-content performed here revealed a chemical evolution with distinct features. In particular above 10–15 at. % of Si, different chemical states were detected for the nitrogen atoms and the chemical state of the Si atoms, was found to be similar to that in bulk silicon nitride. This suggests the existence of separate composition phases in Al–Si–N films, but the exact nature of these phases could not be clarified from our XPS data. At low Si contents chemical shifts and line broadening effects were observed but the distinction between an Al–Si–N solid solution and a phase separation in the Al–Si–N ternary system was not possible. In contrast to our previous XRD investigation that revealed a solubility limit of 6 at. % of Si in aluminum nitride, a correspondingly distinct change in the chemical environment at the solubility limit could not be observed in our XPS data.

The XPS study of the Al–Si–N films presented here illustrates the limitation of XPS analysis for the study of the chemistry of complex multielement nanocomposite coatings. The chemical states of elements contained in the minority phases (typically intergranular layers) can be considerably influenced by the majority (nanocrystalline) phase, such that their chemical state differs from that of a bulk material of same composition.

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