Properties of reactive sputtered alumina-silica mixtures

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Standard antireflective coatings applied to hard substrates like sapphire suffer from poor abrasion resistance. Silica is used as low refractive index layer in many multilayer systems although it has a lower hardness than the substrate. In this work an attempt was done to enhance the hardness by the addition of alumina. Magnetron sputtering was used in two different ways because it delivers dense coatings with high durability. Nanoindention hardness measurements of mixed alumina-silica films are presented in comparison to haze measurements after sand trickling test. The hardness of silica is unexpectedly lowered by the addition of small amounts of alumina. Two different stacks were coated whereas the low refractive index layers were sputtered as pure material and a material mixture. The thickness loss results after an oscillation abrasion test are presented.

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1. Introduction

Devices in everyday use, like watch dials or mobile phone displays are protected by hard glasses. Very often sapphire is used for this purpose because of the high hardness and scratch resistance. As these glasses manufactured from grown and polished crystalline sapphire also have a high refractive index of $n(550\ \text{nm}) = 1.77$ [1] they posses a high reflection of $R = 7,7\%$ per surface. High quality products have antireflection coated sapphire glasses to improve the visibility of the watch dial or display. Usually five layer stacks are used for a visible range antireflection coating from 400-700 nm. The outside antireflection coating is exposed to impacts, scratches and friction. The low refractive index material, which usually is silica, has to be the topmost layer due to the interference design. For this reason the stack has a lower scratch resistance than the substrate. Reference values for mid-frequency sputtered silica on slide glass are $n(550\ \text{nm}) = 1.46 - 1.47$ and a nanoindention hardness of 4...8 GPa depending on the process pressure [2].

Within the EU-project "NoScratch - Process and material research for ultra-stable antireflective coatings on glass" low refractive index materials are developed for the top layer [3]. The approach is the mixing of silica and alumina. Thin alumina coatings have a better wear resistance compared to silica, niobia and tantala on glass substrates [6]. Thick alumina films are used for cutting tools because of the high wear resistance which is, for example, shown for cemented carbides by Skogsmo [4] and Vuorinen [5]. Those films can reach high hardness by different magnetron sputtering techniques when the crystalline α-phase is built. The α-phase was demonstrated on cemented carbides using bipolar pulsed magnetron sputtering [7, 8] with an nanoindention hardness of 22 GPa, reactive magnetron sputtering with an hardness of 23 GPa, with bias even 27 GPa [9] and High power impulse magnetron sputtering [10]. Other groups have also shown the crystal phase on steel [7, 11] or silicon wafers [9, 12] with similar hardnesses. Bobzin et al. [13] reached 25.8 GPa on tungsten carbide. The authors of this work are not aware of any publication on alumina coatings with α-phase, such a high hardness on glass or sapphire substrates

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and with smaller layer thickness that can be used for interference coatings. Schneider et al. [14] published a refractive index of $n(550\ \text{nm}) = 1.65$ and 11.1 GPa for the deposition on optical glass slides.
Even the refractive index of pure, amorphous alumina layers is too high for an antireflection coating. Depending on the process refractive indices from 1.63 to 1.69 are reported for coatings on silicon wafers or metal substrates [15–17]. An antireflective stack design with alumina as low refractive index material would need more layers for a low residual reflectance. More layers result in longer process times and are not suitable for mass production of antireflective coatings. Thus only small amounts of alumina can be mixed in the silica. In the present work we demonstrate the effects of bias and heating on the material properties of these alumina-silica mixtures.

2. Experimental

The dual magnetron setup of a modified Balzes-Pfeiffer PLS 580 (fig. 1) batch coater with one target silicon (5N) and one target aluminum (5N) was used for the deposition of the mixtures. The mixture fraction was tuned in three steps by different pulse lengths for each target: 5 μs Al - 10 μs Si, 5 μs Al - 5 μs Si, 10 μs Al - 5 μs Si. The targets were sputtered in reactive mode with the oxygen partial pressure controlled by a lambda probe. The working point was stabilized by the variation of the off-time. A Melec Spik1000A pulse generator was tuned by the IfU Diagnostic Systems Pulse Pattern Controller for these coatings. The resulting frequency was between 15 and 30 kHz. The bias frequency always doubled by virtue of synchronized pulses. Another mixture was realized by the use of a 40 kHz mid-frequency sine-wave sputter generator from an Advanced Energy PE 10K. The reference samples with pure silicon oxide and aluminum oxide were deposited with both targets equipped with the same material and were also powered by the sine-wave generator. In this case the bias was unsyncronized pulsed dc from an Advanced energy Pinnacle+ with 50 kHz. For further details on the setup and mixture of oxides by tuning the pulse lengths see [18, 19].
Three different substrate environments were realized in one deposition run. The rotating drum in the deposition chamber was equipped with bias for two and heater for one substrate position. This way the samples were in the following environments by rotation of the drum with 15 rpm:

- Floating potential, process temperature;
- Pulsed bias −75 V, process temperature;
- Pulsed bias −75 V, heated substrate plate with > 450 °C.

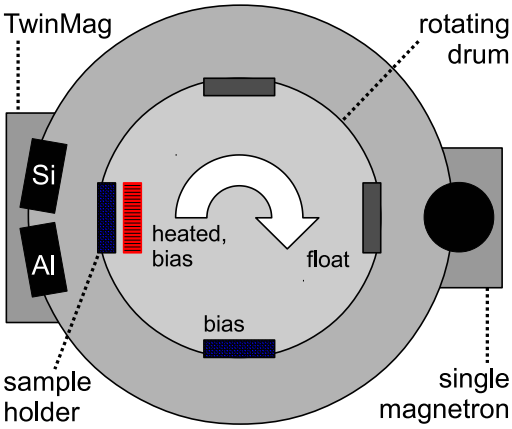

Fig. 1. Sputter system Balzers-Pfeiffer PLS 580 with three different deposition stations in the rotating drum.

The sample plates, without additional heating, had a temperature of 100 to 150 °C. The tempeature of the heated substrate plate was measured in the upper edge during the deposition and was higher than > 450 °C. Static temperature measurements without deposition directly on the substrates gave values 50 − 100 °C higher. Two sapphire substrates were coated with a layer thickness of 300-400 nm at each position. One substrate was transparent and the other one was backside matted for reflectance and ellipsometric measurements. At the process temperature positions pieces of silicon wafers (100) were coated for reference, but all given values in the figures in this paper are measured on sapphire.
An additional sample set for fig. 5 was deposited using the EOSS® which is described in more detail by Rademacher et al. in [20, 21]. In this machine the cylindrical targets are sputtered in pure argon atmosphere and the very thin metallic layers are oxidized by a plasma source afterwards. In our case the first double cylindrical magnetron source was equipped with silicon and the second one with aluminum targets. During the deposition both sources were running on different power fractions to realize the mixtures. The substrate heater was running at 300 °C. On this machine sapphire substrates were coated with a layer thickness of approximatly 400 nm as well. This sample set was created to ensure that the findings are rather material and not system specific.

The hardness was measured by Oliver and Pharr method [22] by nanoindention directly on the sapphire substrates. Mixture composition of the PLS 580 samples was determined by electron probe micro analysis (EPMA) on copper substrates. The given fractions were calculated by the detected aluminum and silicon amounts. In case of the EOSS® samples, the given mixture fraction was only calculated by the power ratio. Refractive index and thickness determination was done by spectral ellipsometry using a Sentech instruments SENResearch SE 850 DUV-NIR with attached micro-spots in the wavelength range of $380-900$ nm. For the sapphire substrates a Sellmeier model [23] and for the layers a Drude-Lorentz model [24] was used inside the SpectraRay3 analysis software.
The abrasive characterization was realized by the oscillating abrasion test (in our test procedure also known as enforced Bayer-test) and the sand trickling test by use of corundum F46 as test medium. For further details on the tests see [6]. The haze values were measured before and after the sand trickling by a BYK haze-gard plus that gives an integrated value for the visible wavelength region. The thickness loss of the top layer after the oscillating abrasion test was identified by ellipsometry. The reflectance was measured with the URA assembly at a Perkin Elmer Lambda 950.

3. Results and Discussion

Six different mixtures, from pure silica to pure alumina, were prepared on the PLS 580 system. The resulting refractive indices for the 18 samples were plotted in fig. 2. The deviations of fractions of sample mixtures from one run were below 2.5 % as determined by EPMA. The fraction value in the diagram was calculated as an average of the samples at floating potential position and biased position. This way the samples from one run can easily be identified because samples plotted with same fraction of alumina are from the same run.

The refractive index range shows typical values between sputtered silica and amorphous alumina coatings. The values of pure materials are somewhat lower than given by Ruske et al. [2] for SiO_2 with $n(550\text{ nm}) = 1.46$ and Schneider et al. [14] for Al_2O_3 with $n(550\text{ nm}) = 1.65$. Reference measurements on silicon substrates from the same deposition run gave refractive index values that are $0.02-0.03$ higher and correspond to the literature values.

The hardness for all samples is shown in fig. 3. The sample from the heated position always has the highest hardness. The process temperature sample

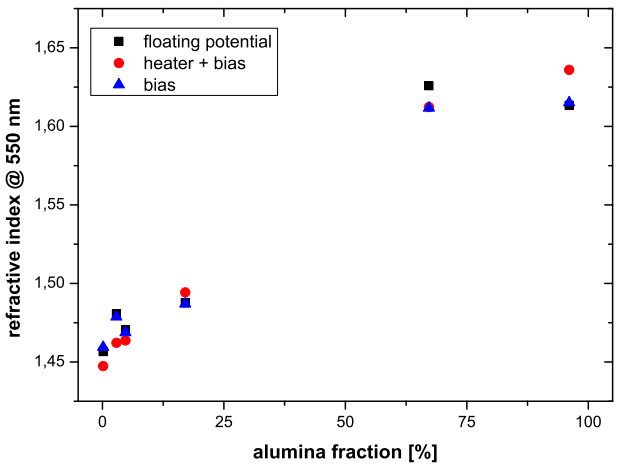

Fig. 2. Refractive index measured on backside matted sapphire plotted against alumina content in silica films.

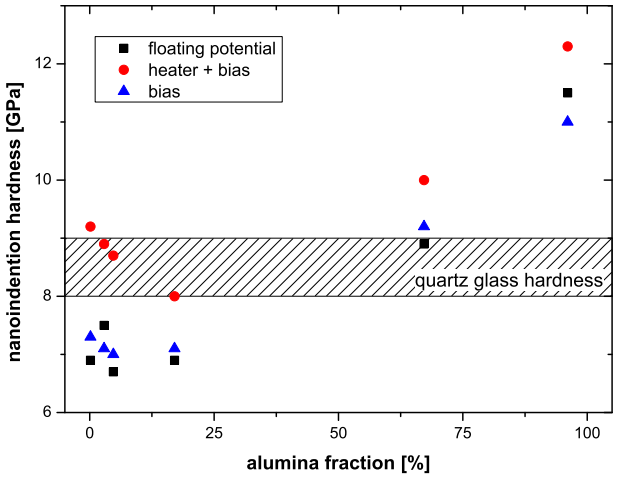

Fig. 3. Nanoindention hardness plotted against alumina content in silica films.

with bias has higher hardness in most cases than the process temperature sample on floating potential. The synchronized bias frequency had a maximum of 60 kHz resulting from the bipolar sputter frequency of 15 to 30 kHz. The influence of bias with low frequencies to insulating substrates with 1 mm thickness was expected to be rather little.
All films have a much lower hardness than the pure sapphire substrate which has a nanoindention hardness of $30,5 \pm 0,8$ GPa. The hardness is lowered for small amounts of alumina in the silica coatings. Only high amounts of alumina lead to enhanced hardness relative to pure silica. This is obvious for the heated samples; but the other samples seem to behave this way also. Spot tests with x-ray

diffraction in grazing incidence mode did only show amorphous films over the whole fraction range. The hardness of pure alumina coatings on process temperature substrates fits well to the value published by Schneider et al. [14] while the heated sample has a little higher hardness. The same applies to the values by Ruske et al. [2] for SiO_2.

The haze increase due to the sand trickling test

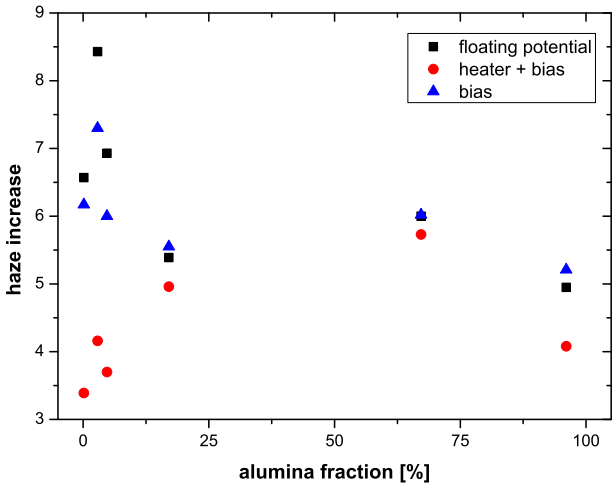

Fig. 4. Haze increase after sand trickling test plotted against alumina content in silica films.

for all samples is shown in fig. 4. The lowest values were found for pure alumina for the floating potential and biased deposition environments at process temperature. For the heated and biased samples the nearly pure silica layers are a little more resistant to the sand trickling test. The highest values were found for sample prapared at process temperature with small alumina content. The haze of the heated samples is following more or less the hardness changes with the fraction. For the other two series this behavior is not that clear. The haze values of the mixtures with low alumina content have a bigger spread than the hardness values for those samples. Hence, for those samples the hardness is not the main material property that influences the sand trickling resistance.

A very similar behavior was observed for the films that were deposited on the production scale and fully automized system EOSS® as shown in fig. 5. In this case the fraction of alumina in the silica films was only varied to about 50 %. Again the silica-rich samples show a lower increase of haze as well as higher hardness than those samples with proceeding alumina content. The hardness is lowered at a higher alumina fraction than for the PLS 580 sam-

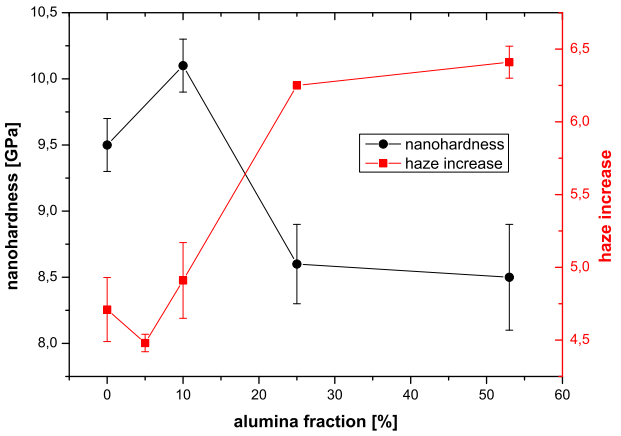

Fig. 5. Nanonindention hardness and haze increase after sand trickling test of alumina-silica mixtures deposited on the EOSS®. The fraction values were calculated by the power ratio of the sputter sources.

ples; but this can also be due to another ratio in the films than calculated by the powers. Thus the material properties hardness and haze increase after sand trickling are influenced more likely by the mixture, than by the deposition process itself.

5-layer stacks were deposited on the PLS 580 with

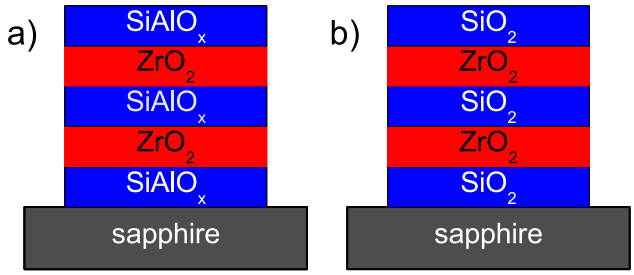

Fig. 6. 5-layer stacks for abrasion resistance characterisation with a) silica-alumina mixture and b) silica as low refractive index material.

a) an alumina-silica mixture and b) pure silica for the low refractive index material (fig. 6). The influence of substrate heating is demonstrated by the example of a little alumina content in the silica thin films (5 μs pulse length at the aluminum and 10 μs pulse length at the silicon target). In these stacks pulsed-DC sputtered Zirconia was used as high refractive index material. The layer thicknesses were chosen with respect to the antireflection effect. In one deposition run two different sample sets were coated: first set at the temperature resulting from the process and the second set heated to 400 °C. This results in different thicknesses of the layers on

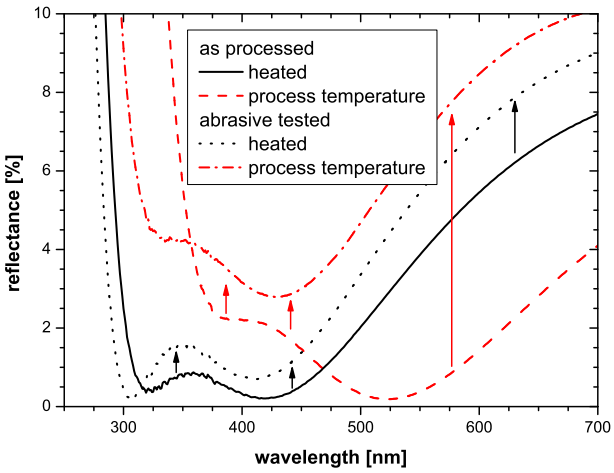

Fig. 7. Reflectance of 5-layer stacks as deposited on the PLS 580 and after oscillating abrasion test.

the two sample sets and also different residual reflectance as shown in fig. 7. The coated samples were tested using the oscillating abrasion test and the thickness loss of the top layer was measured by ellipsometry. The thickness loss on the sample at process temperature was 38 nm and on the heated sample only 6 nm. Thus the reflectance of the heated sample is much lower after the abrasion test. The haze increase is 5.5 for the process temperature and 4.1 for the heated sample.
The stack with silica as low refractive index material has a thickness loss of 8 nm for both the heated and the process temperature sample. The haze increase again is lower for the heated sample with 4.5 and 5.8 for the process temperature sample.
Thus the heated sample with the mixed low refractive index layer has only a slightly better performance than the standard silica top layer. The haze values are in good agreement with the values measured on the single films.

4. Conclusion

23 alumina-silica mixture samples with temperatures ranging from 100 °C to 500 °C and different substrate potentials were deposited and characterized on sapphire substrates. Two different deposition systems with reactive bipolar pulsed magnetron sputtering and metal mode reactive sputtering were used. The resulting hardness of mixed thin films is not linear from pure silica to pure alumina and the total hardness is lower than realized on silicon and carbides. A minimum hardness is realized somewhere between 20 and 60 %. The refractive index of alumina-silica mixtures with a larger alumina fraction is too high. Only fractions of alumina below approx. 40 % resulting in a refractive index of $n(550\ \text{nm}) < 1.55$ can be used for antireflection coatings with low residual reflectance. Thus the mixtures are not suitable to enhance the durability of antireflection coatings against the sand trickling test.
Four different 5-layer stacks were deposited with similar layer thicknesses like used for an antireflection coating. The heated sample with a low amount of alumina in the silica showed a small improvement regarding the thickness loss by the oscillating abrasion test.
As an overall conclusion the heating (and optionally biasing) of the pure silica samples to temperatures of approx. 500 °C has a larger influence on the abrasion resistance than the mixture is able to.

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