Microstructure and Properties of Nanocomposite Al-Si-N System Coatings Produced by Magnetron Sputtering

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Abstract. The paper presents the results of investigations of the structural and phase conditions, mechanical and optical properties of Al-Si-N system coating obtained by magnetron sputtering. The thickness of this coating ranges from 3 to 19 μm and is sprayed on silica glass using magnetron sputtering technique. The formation of nanoscale AlN single phase with HCP crystal system and the crystal grain size of up to 20 nm is discovered using the X-ray diffraction method. The texture of [002] orientation is observed in the structure of Al-Si-N-based coatings. These coatings are characterized by high values of microhardness and coefficient of restitution. The transmission spectrum of the coatings are produced within the range of 190-1100 nm. Al-Si-N-based coatings are characterized by a high degree of transparency (≈ 80%) within the visible light spectrum and complete opaqueness in the ultraviolet region. The refractive index and the thickness of Al-Si-N system coating are determined using the transmission spectrum and refractive index. The refractive index of Al-Si-N-coated glass samples is determined using the transmission spectrum the value of which increases with the increase in the coating thickness.

INTRODUCTION

One of the most promising methods to increase the service life and improve the efficiency of glass parts of products is the protective coating produced by magnetron sputtering technique. Magnetron sputtering technique is widely used to obtain dense and uniform coatings with high adhesion. Coatings based on Al-Si-N system can be used as protection for optical systems. These coatings have a high degree of transparency within the visible light spectrum at certain component ratios and possess a high level of mechanical properties. Presently, a number of works [1-3] is devoted to transparent nanocomposite coatings based on Al-Si-N system produced by magnetron sputtering technique and their properties depending on the process conditions. In the works of Pélisson *et al.* [1, 2], the evolution of Al-Si-N-based coating microstructure is studied under the conditions of increased Si content. It is shown that AlN coating which does not contain silicon, has a columnar microstructure the columns of which are mostly of [002] orientation and extend over the coating thickness. Their width and length decrease with the increase of Si content. In case Si concentration is over 10 at.%, the column structure is not observed, while the morphology of coatings is nanocrystal or amorphous. The obtained Al-Si-N samples are optically transparent

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within the visible light spectrum and opaque within the ultraviolet region. At the same time, Si concentration does not affect the absorption process. Nanohardness measurements show 30 GPa maximum hardness for Al-Si-N system coating containing 10 at.% Si. In the work of Liu *et al.* [3], the optically transparent nanocomposite Al-Si-N-based coating with varying Si content is produced using the magnetron sputtering technique. It is shown that the majority of coatings have AlN crystalline structure with Al-Si-N-phase preferred orientation varying between [110] and [100] directions that is inconsistent with the data obtained in the work of Pélisson *et al.* [1,2]. The maximum hardness of 27.5 GPa is observed in Al-Si-N-based coatings with 25 at.% Si content or higher. Thus, the obtained coatings are transparent in a wide wavelength range of 0.3–9 μm.

It should be noted that in works [1–3], Al-Si-N magnetron sputtering is characterized by the high values of microhardness and coefficient of transparency within the visible light spectrum. At the same time, these coatings have relatively low thickness (1 and 1.5 μm) that restricts drastically the scope of their efficient applications. Until now, Al-Si-N system coatings have been investigated in terms of their potential use in optically-transparent hard coatings resistant to oxidation [2], wear resistant [4, 5] or flexible hard coartings [6, 7]. First of all, interesting is a possible use of Al-Si-N system coatings in the vehicle glass part protection from mechanical shock damages. Besides the high hardness and transparency within visible light spectrum, the important role in this case plays the thickness of protective coatings. Previously in [8], it was shown that the coating thickness increase from 0.9 to 6.2 μm allows improving the protective properties of silica glass due to 1.5 times reduction of the packing density of craters generated by hypervelocity impacts of iron particles. On the other hand, the functional properties of these coatings depend on their real structure (grain size, phase composition, internal stress level, *etc*.). This work focuses on the study of the structural and phase conditions and mechanical-and-physical properties of Al-Si-N-based coatings obtained by pulsed magnetron sputtering.

MATERIALS AND METHODS

The type KV polished silica glass was used as substrates for sputtering Al-Si-N system coating. The coating was carried out on the vacuum installation UVN-05MI 'KVANT' [9]. It was sprayed using the pulse magnetron sputtering on mosaic targets based on aluminum with silicon inserts. A bipolar pulsed source with 50 kHz frequency was used to supply the magnetron with maximum 1.2 kW voltage. Nitrogen partial pressure in the chamber was 0.075 Pa; the total pressure of gas mixture was 0.3 Pa. The substrate temperature during magnetron sputtering was 560±15 K.

The variable parameters during the sputtering Al-Si-N system coating on silica glass substrates was the time of deposition ranging from 90 to 320 min allowing to change the coating thickness (Table 1). The gravimetrical method was used to control the coating thickness based on weighting the sample before and after the magnetron sputtering.

The measurements of the coating elementary composition were made with LEO EVO-50XVP scanning electron microscope (SEM) equipped with an INCA Energy (Oxford Instruments) microanalyzer system. The structural and phase conditions of the samples were investigated on DRON-7 diffractometer using the CoK_α radiation and a 2θ scan rate and Bragg-Brentano X-ray optical scheme (λ= 1.78897 A). The ICDD-JCPDS PDF-2 powder diffraction database was used to identify crystalline phases. The size of coherent scattering regions (CSR) in coatings was determined by Scherrer ratio [10]. To estimate the texture of obtained magnetron sputtering of Al-Si-N system coating, the texture coefficient was calculated by

$$T_C = \frac{I_n(hkl) / I_0(hkl)}{\frac{1}{M}\sum I_n(hkl) / I_0(hkl)},$$

where $I_n(hkl)$ is the reflection intensity (*hkl*); $I_0(hkl)$ is the standard intensity according to the JCPDS (Card N 25-1133); *M* is the number of reflections used in the calculation (where $M = 6$), (*hkl*) reflections include (100), (002), (101) (102) (110) and (103).

The mechanical properties of coatings and silica glass substrates were explored on Nanotest 600 measuring equipment using the instrumented indentation method. Measurements were carried out under 20 mN load and 220 nm indentation depth. In order to obtain the reliable results for each sample, not less than 10 indents were made, and the arithmetic mean value was the final result. The analysis of the unloading leg of the indentation diagram obtained by Oliver-Pharr method provided calculations of microhardness and Yong's modulus [11].

The analysis of the optical properties of Al-Si-N system coating was based on measurements of transmittance factor $T = f(\lambda)$ within the optical wavelength range of λ = 200-900 nm using the SF-256 UVI spectrophotometer (LOMO Photonika). The SF-256 UVI operation is based on measuring the ratio between the two light fluxes passing through the investigated and the standard samples, respectively. The type KV polished silica glass was used as a standard sample.

RESULTS AND DISCUSSION

The selected conditions of magnetron sputtering provide the formation of Al-Si-N-based coating on the surface of the silica glass sample. The coating has different thickness characterized by the elemental composition given in Table 1. According to this table, the quantitative content of silicon, aluminum and nitrogen in the surfaces varies during the increase of the time period of magnetron sputtering. The ratio of the aluminum and silicon atoms remains constant (Al/Si $\approx$ 3) in all coatings obtained.

TABLE 1. The elemental composition of Al-Si-N coatings formed on the type KV polished silica glass surface

Samples	Deposition time, min	Coating thickness (measured) h, μm	Components			Al/Si ratio
			Si [at.%]	Al [at.%]	N [at.%]	
AlSiN -90	90	4.3	12 ± 0.15	37 ± 0.58	51 ± 0.72	3.1
AlSiN -240	240	14.1	10 ± 0.14	29 ± 0.44	61 ± 0.56	2.9
AlSiN -320	320	20.5	9 ± 0.26	25 ± 0.76	66 ± 1.13	2.8

The diffraction patterns for the silica glass samples with Al-Si-N-based coating of different thickness are presented in Fig. 1. In all samples, the diffraction maximums correspond to hexagonal AlN phase of wurtzite type (JCPDS Card N 25-1133). However, AlN diffraction maximums shift to the large angles, and the thicker the coating the larger shift. Hence, aluminum nitride formed in all the samples has the lower lattice parameter (see Table 2) than the standard AlN has (a = 0.3111 nm; c = 0.4979 nm).

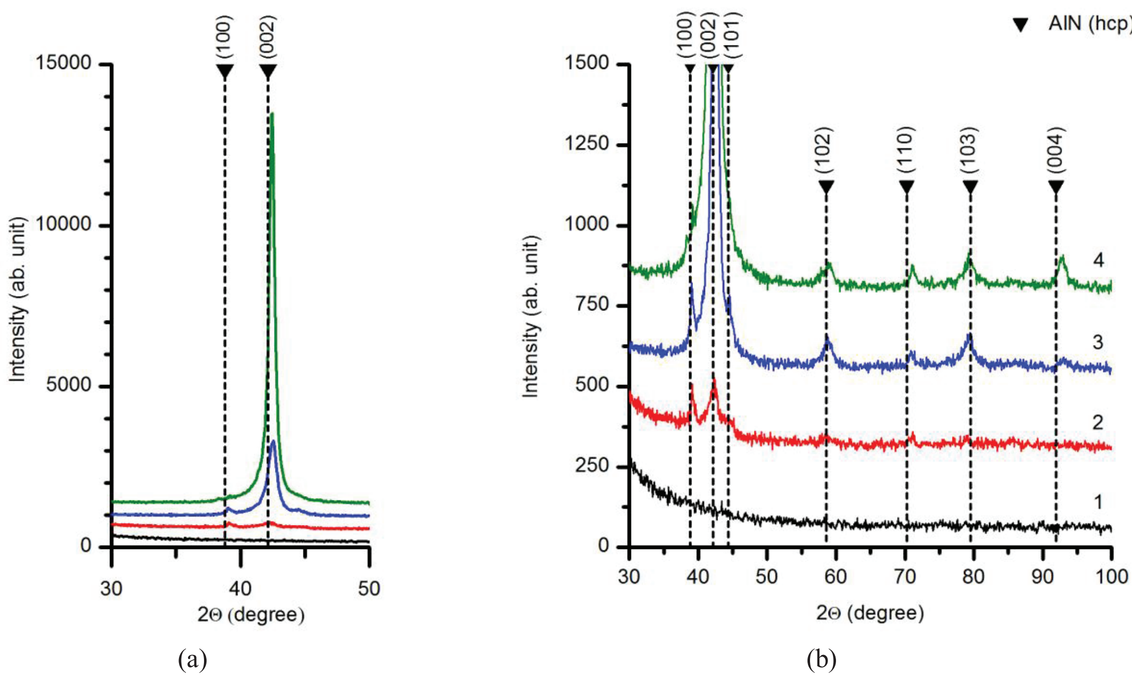

FIGURE 1. XRD patterns of silica glass samples with Al-Si-N-based coating in CoK_α radiation: *1* – KV glass type; *2* – AlSiN- 90; *3* – AlSiN - 240; *4* – AlSiN -320

TABLE 2. Structural parameters of Al-Si-N-based coatings on KV-type silica glass surface

Samples	Coating thickness (measured) h, μm	Lattice parameters of AlN		CSR, nm	Packing density	Coating density, g/cm^3
		a, A	*c*, A			
AlSiN-90	4.3	3.0818	4.9705	10	0.93	3.02
SiAlN-240	14.1	3.0889	4.9354	12	0.96	3.12
AlSiN-320	20.5	3.0793	4.9441	20	1.10	3.62

The analysis of the diffraction patterns of the three samples shows a significant increase in the integral intensity of (002) diffraction line in AlN (Fig. 1a) for the Al-Si-N-based coatings of different thickness. This indicates that the selected conditions of magnetron sputtering facilitate the formation of Al-Si-N-based coatings with pronounced texture on the silica glass substrates. According to Fig. 2, the behavior of the texture coefficient for (100) and (002) diffraction lines indicates to a higher degree of texturing in [002] direction with the increase in time of magnetron sputtering from 90 to 320 min. A presence of the texture in [002] direction also denotes perpendicularity of the hexagonal AlN polar axis to the substrate surface. Obviously, Al-Si-N system coating obtained by magnetron sputtering has a columnar structure, AlN crystal grain columns being perpendicular to the silica glass plane (Fig. 3).

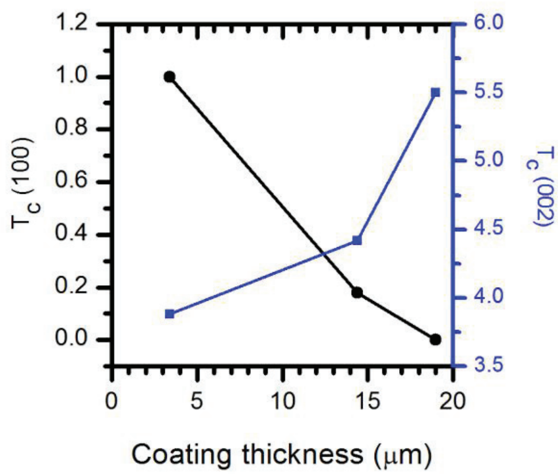

FIGURE 2. Dependence between texture coefficient of (100) and (002) planes and Al-Si-N-based coating thickness

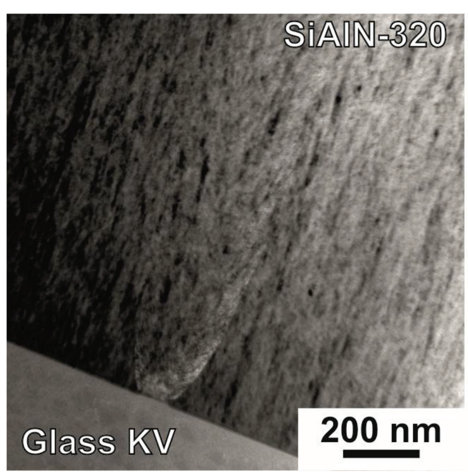

FIGURE 3. TEM bright-field image (cross-section) of nanocomposite microstructure of Al-Si-N-based coating

The CSR of aluminum nitride forming in Al-Si-N system coating is determined by spreading of (002) diffraction line. The results of CSR estimation given in Table 2 show that the finest size of AlN crystal grains is about 10 nm and characteristic to AlSiN-90 coatings having the minimum thickness. During magnetron sputtering, the thickness increase results in the increase of up to 20 nm of CSR in crystalline AlN phase in AlSiN-320 sample. The CSR size values of aluminum nitride manifest rather a high dispersiveness of substructure elements of the sputtered coatings, regardless their thickness.

Figure 4 presents the transmission spectra for silica glass before and after sputtering the coating of different thickness measured in the ultraviolet (UV, λ = 190-380 nm) and visible (IN, λ = 380-780 nm) light spectra. According to Fig. 4, the original silica glass (curve 1) is characterized by a high degree of transparency within the whole wavelength interval. Investigations of the optical transmission spectra of silica glass sputtered with Al-Si-N system coating of different thickness show that within the visible light spectrum, all the samples retain their transparency. However, within the 190-300 nm wavelength interval, the investigated coatings are opaque. Moreover, the absorption limit shifts to longer wavelengths when the coating thickness increases from 4.3 to 20.5 μm. A considerable shift of the absorption limit on transmission spectra to the longer waves observed during the thickness increase can be associated with the growth of AlN nanoclystal grain size. It is known, that the position of the absorption limit of materials depends on the band structure and is determined by the band gap. Thus, the absorption limit of semiconductors with Eg = 2.5 ÷ 3 eV band gap is found within the visible light spectrum, while that of dielectrics with Eg> 3 eV, it is found within the ultraviolet region. A number of factors, including the grain size, significantly affect the band gap in semiconductors. In works of [12, 13] it is shown that the decrease in the particle or crystal size leads to the increase in the band gap. Since with the growth of AlN crystal grain size from 10 to 20 μm increases the coating thickness from 3 to 10 μm (Table 2), one can assume that its band gap should reduce. To confirm this assumption, the band gap is analyzed using the methodology suggested in [14]. The results of this analysis show that the band gap reduces from 2.38 eV (d_{CSR} =10 nm) to 1.68 eV (d_{CSR} =20 nm) during the transition from AlSiN-90 to AlSiN-320 sample. However, for more accurate estimations, it is necessary to carry out additional measurements within the short-wave region.

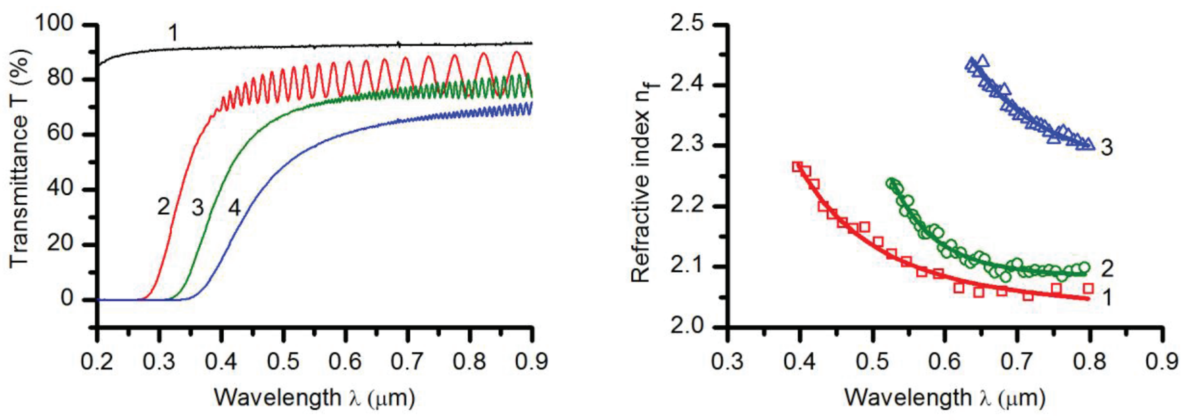

FIGURE 4. Transmittance spectra (a) and dispersion of refractive index (b) of silica glass samples coated with Al-Si-N system: *1* – type KV glass; *2* – AlSiN-90; *3* – AlSiN-240; *4* – AlSiN-320

It should be noted that diffraction maximums and minimums of the transmission spectrum are observed in all silica glass samples with Al-Si-N-based coatings within the visible light spectrum. The arrangement of maximums and minimums of observed oscillations depends on the thickness and refractive index of the coating and the spectral range measured. Thus, Swanepoel method assists in obtaining the refractive index for Al-Si-N-coated silica glass samples using the determined spectral dependences of transmittance factor [15].

The refractive index calculation using Swanepoel method, is based on the construction of diffraction maximums $T_M(\lambda)$ and minimums $T_m(\lambda)$ of the transmission spectrum of the coating deposited to silica glass substrate and further consideration of $T_M(\lambda)$ and $T_m(\lambda)$ curves as continuous functions. Having obtained

$T_M(\lambda)$ and $T_M(\lambda)$ curves, the refractive index n_f of coatings within the range of high transparency can be determined by

$$n_f = \left[N_1 + \left(N_1^2 - n_s^2 \right)^{\frac{1}{2}} \right]^{\frac{1}{2}}, \tag{1}$$

where

$$N_1 = \frac{2n_s}{T_m(\lambda)} - \frac{n_s^2 + 1}{2}. \tag{2}$$

In this case, the substrate refractive index can be obtained from:

$$n_s = \frac{1}{T_s} + \left(\frac{1}{T_s^2} - 1 \right)^{\frac{1}{2}}, \tag{3}$$

where T_s is the substrate transmittance factor almost constant in the region of high transparency. The error of the linear refractive index is ±1%.

Using the experimental spectral T(λ) dependences and equations (1) – (3), the refractive index dispersions can be found within the visible light spectrum for Al-Si-N system coatings of different thickness (Fig. 4b). The points on the presented dependencies indicate the obtained refractive index in the experimental spectrum, while the lines indicate their approximation. Approximation of the experimental points, performed by the empirical Cauchy formula using the least square method, results in the following equations:

$$n_1(\lambda) = 1{,}96 + \frac{0{,}046}{\lambda^2},$$

$$n_2(\lambda) = 1{,}95 + \frac{0{,}071}{\lambda^2},$$

$$n_3(\lambda) = 2{,}05 + \frac{0{,}156}{\lambda^2}.$$

According to Fig. 4b, the refractive index reduces with the increase of the wavelength value in all the coatings, *i.e.* the normal dispersion is observed. In addition, the more the thickness of Al-Si-N-based coating the higher its refractive index (Table 3) within the whole wavelength interval. It is known that the increase of the refractive index during the extending of the coating thickness can be caused by the growth of their packing density. The packing density *p* of the coatings depends on the refractive index [16]:

$$p = \frac{p_f}{p_m} = \frac{n_f^2 - 1}{n_f^2 + 2} \frac{n_m^2 + 2}{n_m^2 - 1}. \tag{4}$$

where n_f and n_m are the refractive indices of the coating and the bulk sample, respectively. Calculation results of the packing density and the density of the investigated coatings are presented in Table 2.

The analysis of extreme values distributed within the transmission spectra, allows estimating not only the refractive index of coatings, but also their thickness. The extreme values of $T_M(\lambda)$ function in case of normal radiation of the sample surface are true if the following condition is satisfied:

$$n_f d = m\frac{\lambda}{4}, \tag{5}$$

where n_f is the refractive index of the coating; *d* is the coating thickness; *m* is the serial number of extreme value; λ is the wavelength corresponding to the extreme value of T_M transmittance factor.

For the determination of the coating thickness, it is necessary to obtain the serial number of extreme *m* value measuring the coordinates of two neighboring extreme (λ_M, λ_{M+2}) values with the even *m* value on the wavelength scale:

$$m = \frac{2 \cdot \lambda_{M+2}}{\lambda_M - \lambda_{M+2}}. \tag{6}$$

The coating thicknesses determined according to the spectrophotometric method using (5) are given in Table 3. For comparison, Table 3 also gives thicknesses of Al-Si-N-based coating measured gravimetrically. The differences identified in results of evaluating by the two different methods, are explained by disadvantages of the gravimetric method. The case is that the gravimetric method implies using the standard density value of the bulk material, namely AlN, although densities of the coating and the bulk material are different. Therefore, for more accurate determination of the coating thickness by the gravimetric method, more research is required to determine the density of the coating material. Consequently, the spectrophotometric method is the most effective non-invasive method for detecting the thickness of optically transparent coatings.

The investigation results of mechanical properties of Al-Si-N-based coatings produced by magnetron sputtering are presented in Table 3. According to this table, the microhardness of Al-Si-N-based coating is 28-30 GPa depending on its thickness and triply exceeds that of the original silica glass.

TABLE 3. The properties of Al-Si-N-based coatings on the type KV silica glass surface

Sample	**Refractive index (λ=0.65 μm)**	**Coating thickness h, μm**		**Microhardness, GPa**	**Young's modulus, GPa**	**Coefficient of restitution W_e**
		measured	**calculated**			
Glass KV	1.48	–	–	9.5	73	0.67
AlSiN-90	2.06	4.3	3.4	27.7	204	0.70
AlSiN-240	2.12	14.1	14.4	28.7	241	0.71
AlSiN-320	2.44	20.5	19.0	30.0	246	0.73

It is known that microhardness of crystalline AlN with the HCP crystal system does not exceed 16 GPa [17]. One can assume that the high microhardness of Al-Si-N-based coating is associated with the formation of AlN phase in the nanostructured state. In addition, a higher microhardness can be conditioned by the high level of residual stresses occurring in coatings with a columnar structure. It is worth noting that in all Al-Si-N-based coatings, the high microhardness is combined with the high coefficient of restitution ($R_e \geq$ 0.70).

CONCLUSIONS

The X-ray diffraction analysis showed that the pulsed magnetron sputtering technique allowed producing Al-Si-N-based coatings on the silica glass surface. The coating possessed different thicknesses comprising AlN phase with HCP crystal system. The thickness of this coating ranged from 3 to 19 μm, and the amount of AlN phase also increased. The most characteristic morphological feature of the coatings was their columnar structure with [002] texture orientation. All the obtained coatings are nanocrystal, since the cross-sectional size of their crystal grains ranged between 10-20 nm depending on the coating thickness.

A study of the optical properties of Al-Si-N system coatings showed that within the visible light spectrum they have a high degree of transparency (80%). The maximum transmittance factor of ~80% is characteristic of AlSiN-90 coatings with the lowest thickness of 3.4 μm. Al-Si-N-based coatings possessed the substantial absorption within the ultraviolet region. Spectrophotometric measurements allowed detecting the refractive indices and the coating thickness. It was found that all Al-Si-N system coatings obtained by pulsed magnetron sputtering had a normal dispersion of the refractive index. The use of Al-Si-N-based coatings not only increases the microhardness of the surface layer, but also retains the high level of elastic properties of the samples.

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