

Analysis of dispersive interactions at polymer/TiAlN interfaces by means of Dynamic Force Spectroscopy

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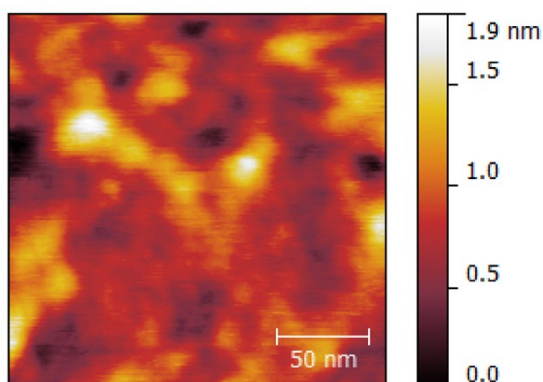
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Supporting Information

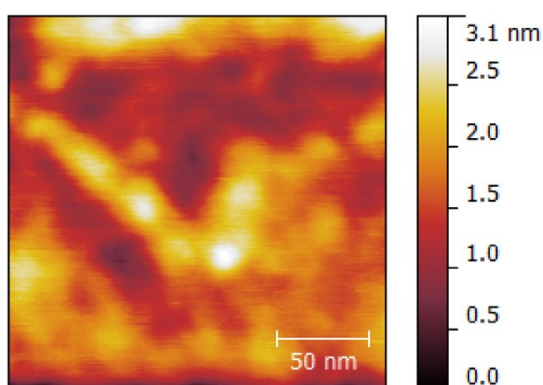
Surface topography of the polymer thin films

The surface topographies of the employed polymer thin films are shown in Figure S 1.

a) PC



b) PS



c) PP-HMDSO

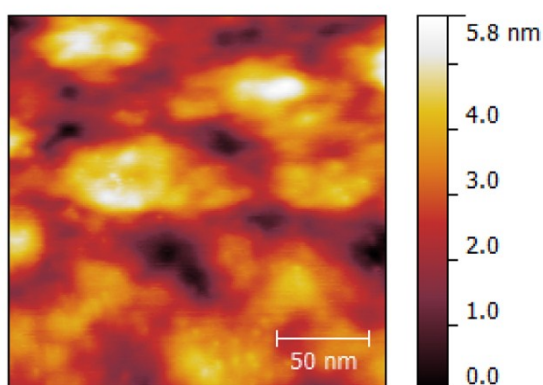


Figure S 1: Non-contact AFM surface topographies of the **a)** PC, **b)** PS and **c)** PP-HMDSO polymer thin films measured with an XSC11 cantilever (Mikromasch, $k = 45 \text{ N m}^{-1}$).

Surface chemical analysis of the polymer thin films by FTIR and XPS

Figure S 2 shows the FTIR spectrum of the PP-HMDSO deposited on an Al mirror and measured in reflection geometry. The bands observed were typical for the HMDSO plasma polymer and were located at 2960 (CH_3 stretch), 2908 (CH_2 stretch), 2154 (Si-H), 1264 (Si-CH_3 sym. deformation), 1107 (Si-O-Si , Si-O-C stretch), 847 (Si-CH_2 sym. rocking) and 809 cm^{-1} (Si-CH_2 asym. rocking).[1] The main building blocks of the PP-HMDSO were therefore Si-H , $\text{Si-CH}_{2/3}$ and Si-O groups.

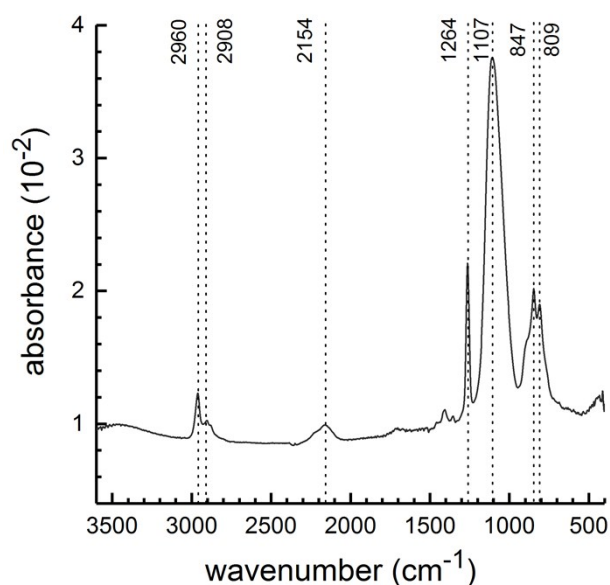


Figure S 2: FTIR of the PP-HMDSO deposited on an Al mirror and measured in reflection geometry.

The XPS stoichiometry of the PP-HMDSO film was as shown in 28 at% O, 40.5 at% C and 31.5 at% Si as shown in Table S 1. Compared with the monomer composition of 11 at% O, 66 at% C and 23 at% Si the O concentration was therefore increased at the expense of the C concentration. This might be a result from oxidation due to residual oxygen present in the plasma chamber.

Table S 1: Surface stoichiometries of the polymer thin films as measured by XPS at an angle of emission of 15° relative to the surface normal.

	C1s / at%	O1s / at%	Si2p / at%
PC	84.8	15.2	-
PS	100	-	-
PP-HMDSO	40.5	28.0	31.5

The high-resolution spectra of PC and PS are shown in Figure S 3. The PC spectrum was described by the CC and CH component at 284.8 eV, the CO component at 286.3 eV, the carbonate at 290.7 eV and the π shake-up at 291.8 eV. The overall atomic stoichiometry was as shown in Table S 1 characterized by 84.8 at% carbon and 15.2 at% oxygen. The lineshape as well as the stoichiometry are in agreement with literature.[2] This situation was also found in the case of the polystyrene sample.[3]

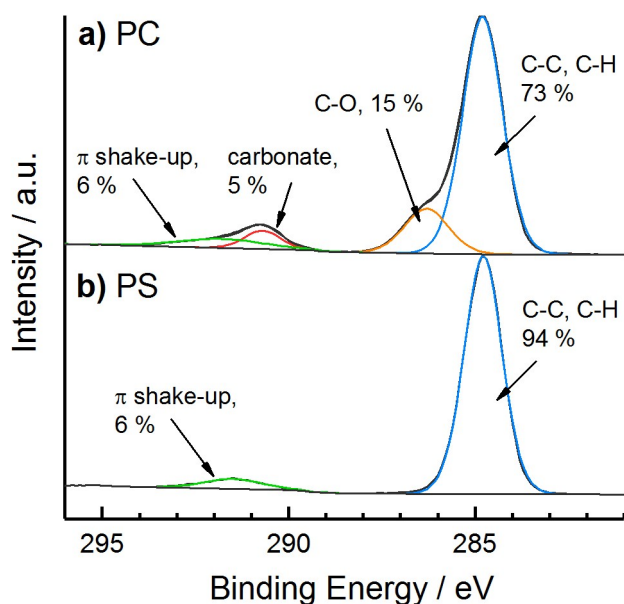


Figure S 3: High resolution XPS spectra of the **a)** PC and **b)** PS thin films measured at an angle of emission of 15° relative to the surface normal. The binding energy scale was corrected for charging by shifting the joint CC and CH component to 284.8 eV. The intensities are normalized and shifted on the ordinate for improved visualization.

XPS of TiAlN and TiAl(O,N)

Figure S 4 shows the high resolution spectra of TiAlN after atmosphere exposure and O beam treatments. The N1s spectrum was described by up to four components located at 395.9, 397.0, 398.4 and 402.0 eV. The components at 395.9 and 397.0 eV are related to TiAl(O,N) and non-oxidized TiAlN according to their binding energies.[4–7] The nature of the satellite component at 398.4 eV is under debate and the relevance of surface N-O compounds or defects is discussed.[8,9] The component at 402.0 eV is commonly assigned to N₂ incorporated into the defective surface oxide film and was observed to represent a main component of the N1s signal after intense oxidation using the O beam at 1.5 kV.[10,11] It is noted that the TiAl(O,N) components of all core level signals could not be correlated inter alia by stoichiometric considerations due to the uncertain composition of the TiAl(O,N) phase.

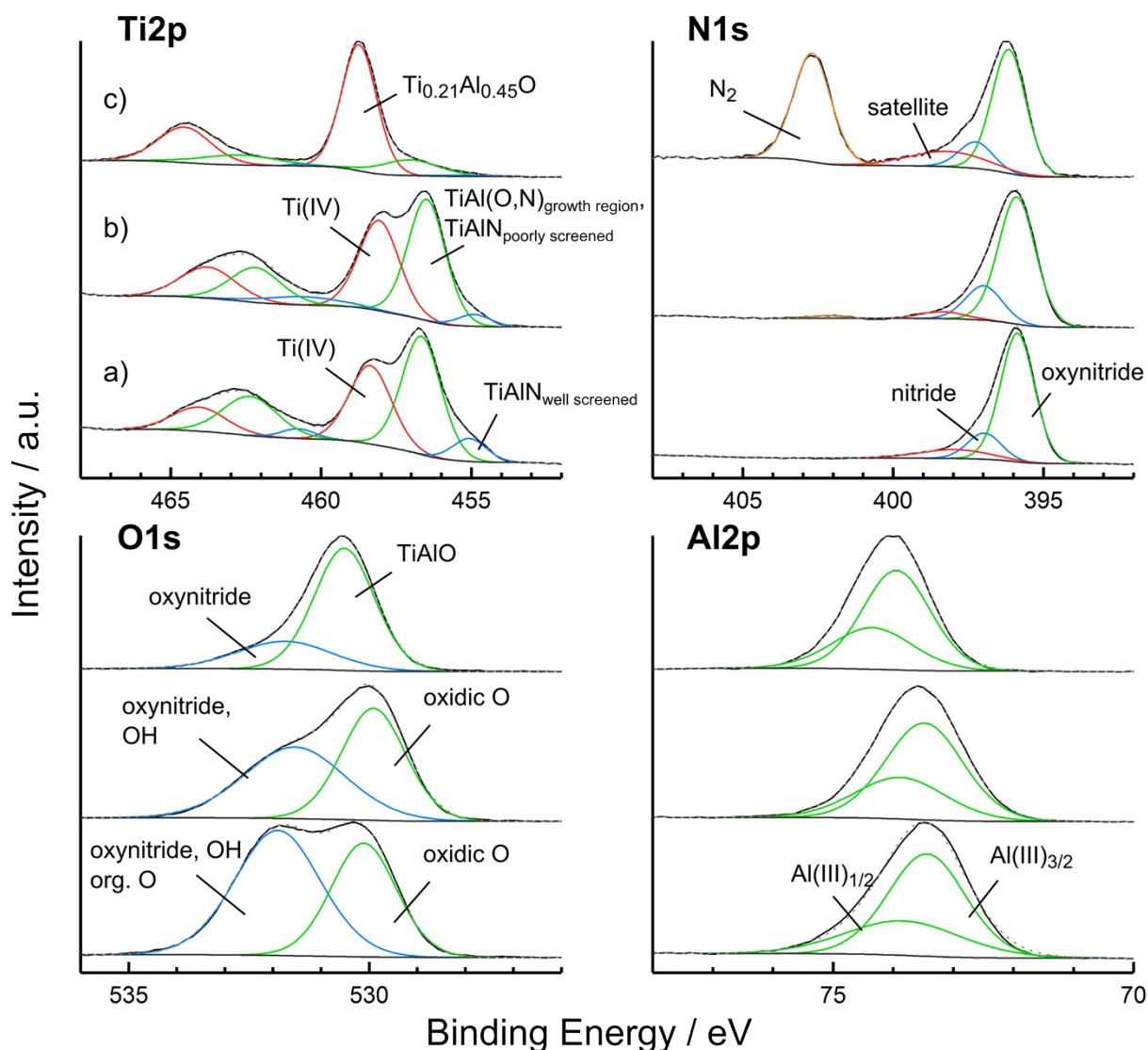


Figure S 4: High resolution core level spectra of **a)** TiAlN after deposition and atmosphere exposure, **b)** after removal of adventitious contaminations using an O beam at 0 eV for 1 min and **c)** after intense oxidation using an O beam at 1.5 kV for 45 s. The intensities are normalized and shifted on the ordinate for improved visualization.

The O1s spectrum of the atmosphere exposed surface was described by two components at 530.0 and 532.0 eV. The component at 530.0 eV was assigned to oxidic oxygen when considering that the O1s binding energy of TiO_2 is 530.0 eV and that of TiAlO is located around 530.6 eV.[12,13] At 532.0 eV several compounds overlap such as TiAl(O,N) , surface hydroxyl groups Ti-OH , Al_2O_3 and adventitious contaminations.[8,9,12,14,15] The modified Auger parameter as determined from the barycentre of the O1s signal obtained after cleansing amounted 1040.8 ± 0.1 eV and is typical for a ternary mixed TiAlO .[13] Thus, segregation of the surface oxide on atmosphere exposed TiAlN into Al_2O_3 and TiO_2 as indicated by the binding energies of the two O1s components was not supported by the investigation of the Auger parameter. Consequently, the precise chemical state of the surface oxide on atmosphere exposed TiAlN could not be entirely resolved based on the spectra investigated.

In this regard, the situation after intense surface oxidation using an O beam at 1.5 kV was unambiguous. The two components of the O1s signal were located at 530.5 eV and 531.8 eV and related to TiAlO and TiAl(O,N) based on their binding energies.[13] The modified Auger parameter was 1040.6 ± 0.1 eV and therefore located within the region of mixed TiAlO .[13]

The Al2p signal was described by two components split due to spin-orbit coupling by 0.4 eV. In the case of atmosphere exposed TiAlN and after surface cleansing the Al2p signal was located at 73.6 eV. After

intense surface oxidation using the O beam at 1.5 kV the Al2p was shifted to 74.0 eV. In this regard, earlier investigations indicated no shift of the Al2p component due to oxidation and this finding might therefore rather be related to structural changes induced by the O beam.[7,9] A more precise deconvolution of the Al2p signal into components related to the oxidic, oxynitridic or nitridic layers could not be performed due to the very similar binding energies of the Al(III) ion in these phases.[7]

Table S 2: Surface composition of TiAl(O,N) in the as deposited and atmosphere exposed state and after surface cleansing using an O beam at 0 eV for 7 min.

treatment	C1s / at%	O1s / at%	N1s / at%	Ti2p / at%	Al2p / at%	Al/Ti
atmosphere exposed	26.0	38.2	8.8	8.4	18.6	2.2
surface cleansed	0.8	49.8	11.0	13.2	25.2	1.9

The stoichiometry of the TiAl(O,N) cantilevers was also investigated on flat samples and the XPS derived stoichiometries of the surfaces in the atmosphere exposed and cleaned state are shown in table s 2. Similar to TiAlN, surface enrichment of Al was observed and the effectiveness of the cleaning procedure using the O beam at 0 V is demonstrated by the reduction of the C1s concentration to below 0.8 at%.

Angle-resolved XPS measurements have been performed on the TiAlN sample after O beam oxidation in order to verify the presence of the $\text{Ti}_{0.21}\text{Al}_{0.45}\text{O}$ layer at the outermost surface. The corresponding Ti2p spectrum is shown in figure S 5 and an increase of the intensity of the $\text{Ti}_{0.21}\text{Al}_{0.45}\text{O}$ component was observed when increasing the angle of emission from 15° to 60° relative to the surface normal. This validates the superficial enrichment of $\text{Ti}_{0.21}\text{Al}_{0.45}\text{O}$.

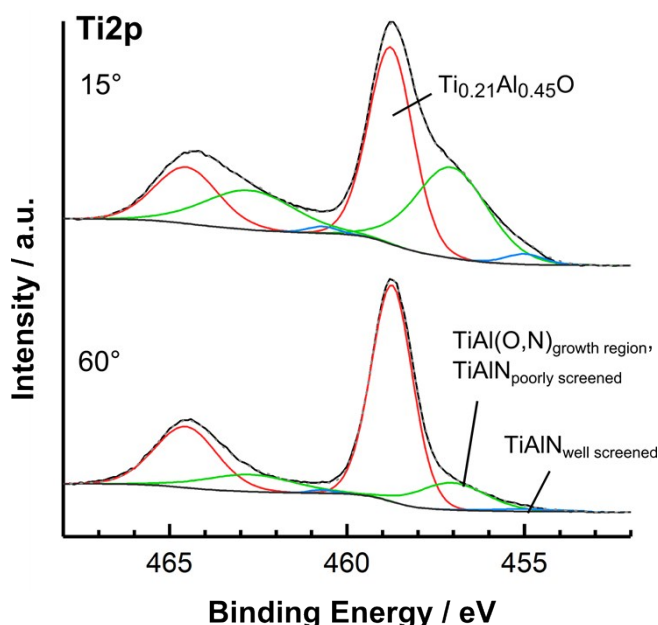


Figure S 5: Angle-resolved XPS of the Ti2p spectrum of TiAlN after O beam oxidation at emission angles of 15° and 60° relative to the surface normal.

The high resolution core level spectra of the TiAl(O,N) surface are shown in figure S 6 and were analysed in analogy to the TiAlN surfaces.

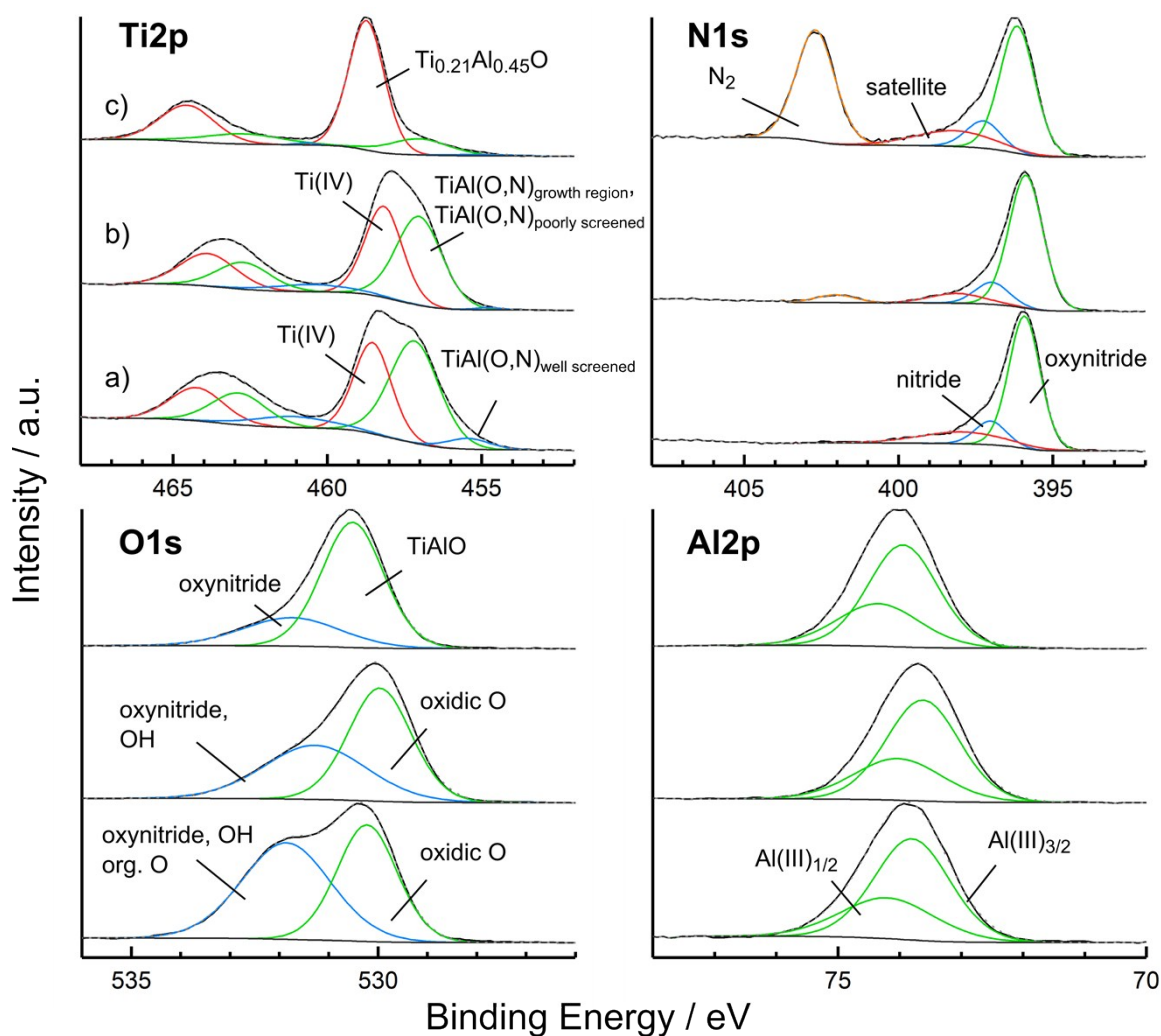


Figure S 6: High resolution core level spectra of **a)** TiAl(O,N) after deposition and atmosphere exposure, **b)** after removal of organic contamination using an O beam at 0 eV for 1 min and **c)** after intense oxidation using an O beam at 1.5 kV for 45 s. The intensities are normalized and shifted on the ordinate for improved visualization.

Electron microscopy images of tips after DFS measurements

This section lists electron microscopy images of the used TiAlN, TiAl(O,N), TiO₂ and Al₂O₃ tips after DFS measurements for documentation of the quality of the tips. The measurements were performed using a FE-SEM (Zeiss Neon 40).

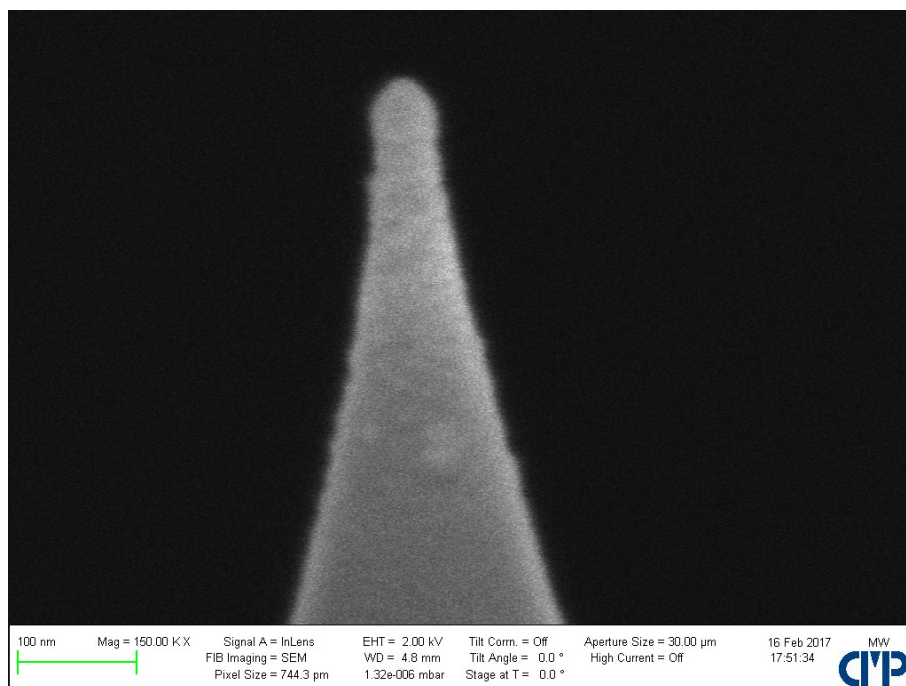


Figure S 7: TiAlN coated tip used within this study after DFS measurements and intense surface oxidation using the O beam at 1.5 kV for 45 s.

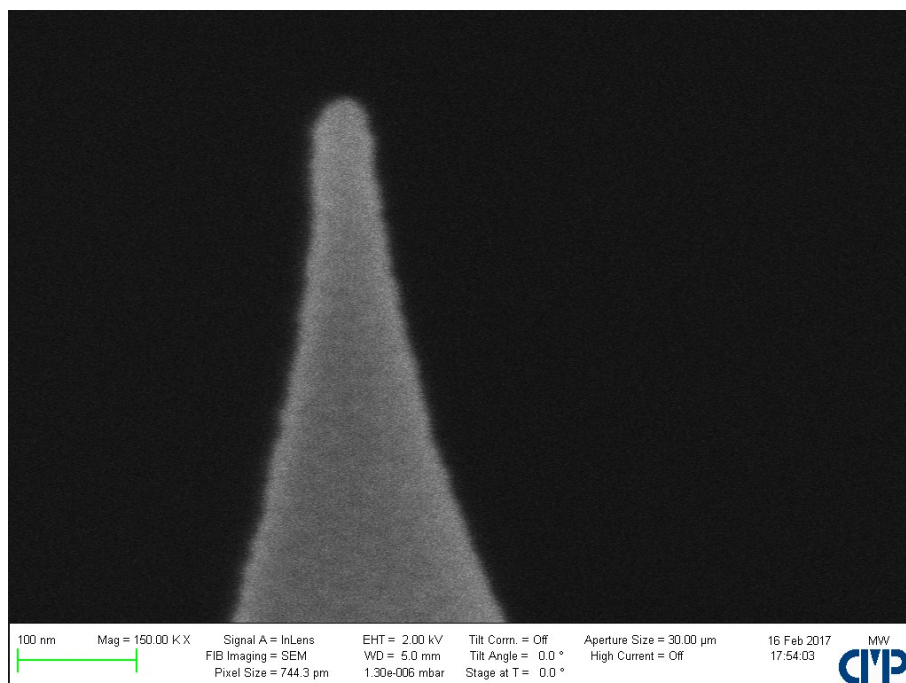


Figure S 8: TiAl(O,N) coated tip used within this study after DFS measurements.

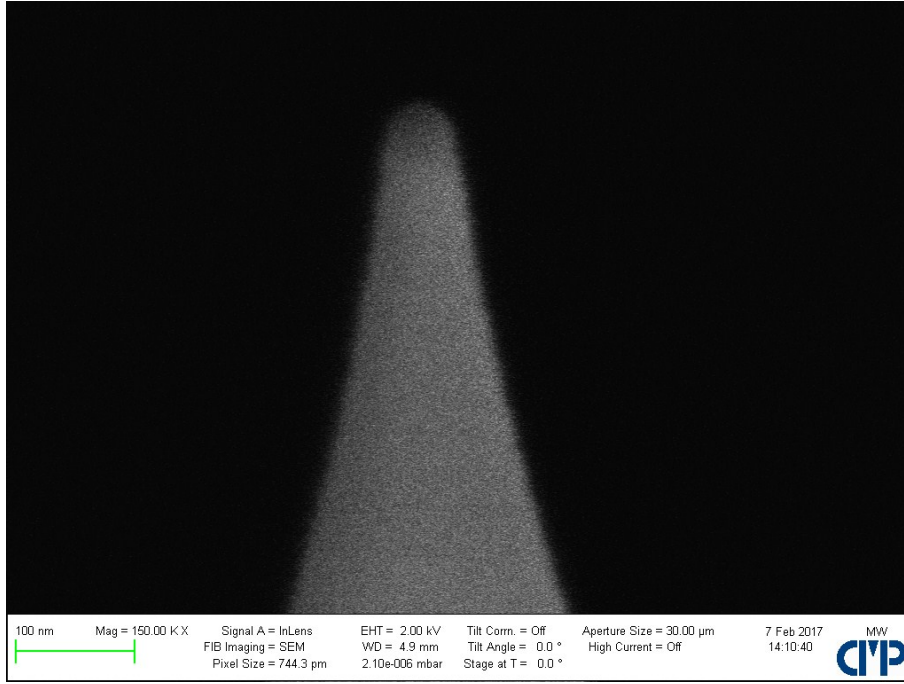


Figure S 9: Al_2O_3 coated tip used in this study after DFS measurements.

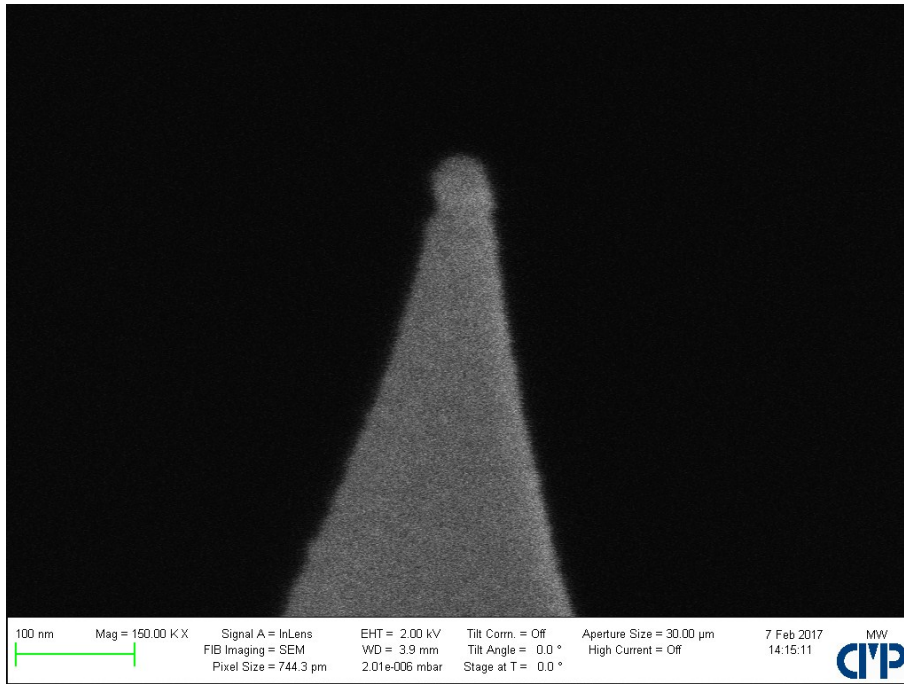


Figure S 10: TiO_2 coated tip used in this study after DFS measurements.

Lifshitz analysis and optical data

Within the QUEELS- $\epsilon(\omega, k)$ -REELS software package the dielectric function is defined by the energy loss function (ELF) as [16–18]

$$\text{Im}\left(-\frac{1}{\epsilon(\omega, k)}\right) = \theta(\hbar\omega - E_g) \cdot f(\hbar\omega) \cdot \sum_i \frac{A_i \gamma_i \hbar\omega}{(\hbar^2 \omega_{0,i}^2(k) - \hbar^2 \omega^2)^2 + \gamma_i^2 \hbar^2 \omega^2} \quad (\text{S1a})$$

$$\hbar\omega_{0,i}(k) = \hbar\omega_{0,i} + \alpha_i \frac{\hbar^2 k^2}{2m_e} \quad (\text{S1b})$$

$$f(\hbar\omega) = \left[\frac{a2(\hbar\omega - E_g)^p}{\hbar^2\omega^2} \right]^{tmp1}, \text{ if } E_g < \hbar\omega < E_g + a1 \quad (S1c)$$

$$tmp1 = \cos^2 \left(\frac{\pi\hbar\omega - E_g}{2a1} \right) \quad (S1d)$$

$$f(\hbar\omega) = 1, \text{ if } \hbar\omega > E_g + a1 \quad (S1e)$$

With $\epsilon(\omega, k)$ being the dielectric function, $\hbar\omega$ the energy, E_g the band gap energy, A_i the strength of oscillator i , γ_i the damping and $\hbar\omega_{0,i}$ the resonance frequency, α_i the momentum dispersion coefficient k the wave vector and m_e the electron mass. $\Theta(\hbar\omega - E_g)$ is a step function, which is unity at $\hbar\omega > E_g$ and zero at $\hbar\omega < E_g$. The function $f(\hbar\omega)$ is introduced to smoothen the region close to the band gap by using the parameters $a1$ and $a2$. The exponent p is 0.5 or 2 for a direct and an indirect band gap.

The oscillator parameters used throughout this study are shown in Table S 3.

Table S 3: Oscillator parameters of polycarbonate, polystyrene, TiO_2 , Al_2O_3 and $Ti_{0.21}Al_{0.45}O$ as determined by REELS.

		$\hbar\omega_0$ / eV	A_0 / eV ²	$\hbar\gamma$ / eV	α
PC		6.8	1.2	0.95	0
E_g	4.2	14.9	6.4	4.9	0
$a1$	3.2	22.2	189.5	13	0
$a2$	9	32.5	184.1	20	0
p	2	27.6	38.7	9	0
PS		7	2.1	1.23	0
E_g	4.2	10	0.5	2	0
$a1$	3.2	13	0.5	2	0
$a2$	9	22.2	206.1	13	0
p	2	27.6	48.2	9	0
		32.5	140.0	18	0
TiO_2		6.2	1.0	3	0.05
E_g	3.2	12	27.5	4.7	0.05
$a1$	1	14.3	18.0	3.7	0.05
$a2$	0.1	17.7	25.8	7	0.05
p	2	25.5	211.5	11	0.05
		31.5	21.0	7	0.05
		38.4	19.8	5	0.05
		46.8	279.8	9	0.05
		52.7	69.6	7	0.05
Al_2O_3		14.4	9.6	6	0.02
E_g	6.3	22.7	210.0	7.8	0.02
$a1$	2	32	271.8	18	0.02
$a2$	0.1				
p	2				
$TiAlO$		5.85	0.4	3	0.05
E_g	3.2	10.2	4.9	3.9	0.05

<i>a1</i>	1.5	14	12.5	5.2	0.05
<i>a2</i>	8	23.2	288.9	14	0.05
<i>p</i>	2	32	51.6	11	0.05
		38.6	28.9	6	0.05
		46.6	167.8	11	0.05
		52.3	56.2	9	0.05
		63	32.7	7	0.05

The Hamaker coefficients were calculated according to [19]

$$A_h(d) = -\frac{3}{2}kT \sum_{n=0}^{\infty} \int_{r_n}^{\infty} x \ln[(1 - \Delta_{Am} \Delta_{Bm} e^{-x})(1 - e^{-x})] dx \quad (S2a)$$

$$\Delta_{im} = \frac{x_m \varepsilon_i - x_i \varepsilon_m}{x_m \varepsilon_i + x_i \varepsilon_m} \quad (S2b)$$

$$x_i^2 = x_m^2 + \left(\frac{2l\xi_n}{c}\right)^2 (\varepsilon_i - \varepsilon_m), x_m = x \quad (S2c)$$

$$r_n = \frac{2l\sqrt{\varepsilon_m}}{c} \xi_n \quad (S2d)$$

$$\hbar \xi_n = 2\pi kTn \quad (S2d)$$

where ξ_n is the n th Matsubara frequency, ε_m the relative permittivity of the medium (vacuum in this case) and r_n is the pertinent ratio, which accounts for retardation.[19] The first term with $n = 0$ in equation S2a is multiplied by 0.5. In equation S2 the dielectric function ε was supplied directly as $\varepsilon(\omega)$ from the QUEELS- $\varepsilon(\omega,k)$ -REELS software package after conversion to the imaginary axis according to the Kramers-Kronig transform

$$\varepsilon(i\xi_n) = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{\omega_R \varepsilon''(\omega_R)}{\omega_R^2 + \xi_n^2} d\omega_R \quad (S3)$$

where ω_R is the radial frequency. The non-retarded constants were obtained as limiting values for low distances around 0.3 nm.

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