# Journal of Materials Chemistry C

## PAPER

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Cite this: J. Mater. Chem. C, 2018, 6, 823

Received 29th September 2017, Accepted 27th December 2017

DOI: 10.1039/c7tc04457g

rsc.li/materials-c

## 1. Introduction

Anti-reflection coatings (ARCs) serve as a critical component in many optical systems to reduce reflection losses, usually by means of destructive interference or a  $\pi$ -phase shift of the reflected beams. This is an integral part of many devices that function by means of absorption or detection of the electromagnetic spectrum. ARCs are frequently applied to photovoltaic devices, for example, for increased light capture and greater power conversion efficiencies.<sup>1–3</sup> Plasma enhanced chemical vapor deposition (PECVD) silicon nitride (SiN<sub>x</sub>) ARCs have become commonplace for direct deposition onto polycrystalline silicon photovoltaics.<sup>4,5</sup> Optical sensors,<sup>6</sup> lasers,<sup>7</sup>

<sup>c</sup> Department of Physics, Virginia Tech, Blacksburg, Virginia 24061, USA.

# Enhanced scratch resistance of self-assembled silica nanoparticle anti-reflection coatings;

Jonathan S. Metzman, 🝺 \* a Guanyu Wang, b John R. Morrisb and James R. Heflin \* cd

The layer-by-layer ionic self-assembly of silica nanoparticles (SiO<sub>2</sub> NPs) and poly(allylamine hydrochloride) (PAH) can yield high-quality, tunable, and cost-effective anti-reflection coatings (ARCs). However, these purely ionic films lack the necessary scratch resistance for long-term stability. The addition of thermallycrosslinking polyelectrolytes, PAH and poly(acrylic acid) (PAA), can provide a solution to this challenge. The improved ARC design involves the formation of repeat-units of PAH/PAA/PAH/SiO<sub>2</sub> interlayer ionic self-assembled multilayers (ISAM) films. This paper examines the associated effects resulting from the manipulation of the PAA pH to result in low to high chain charge densities (pH = 3.0 to 6.0, respectively). This PAA pH alteration dramatically shifts the films' scratch resistance and anti-reflective properties in opposite directions. The films' RMS surface roughness and surface morphology are also found to be substantially affected by the PAA pH variation, especially when the pH is in close proximity to the PAA pKa. In this report, characterization of these properties is obtained through UV-vis spectroscopy, ellipsometry, profilometry, field-emission scanning electron microscopy (FESEM), tribology, macro-scale scratch testing, and haze measurements. The development of covalent amide linkages in PAH/PAA films upon thermal crosslinking is confirmed through Fourier transform infrared spectroscopy. The primary goal of the study is an optimization of the trade-off between scratch resistance and anti-reflection properties within PAH/PAA/PAH/SiO<sub>2</sub> interlayer ISAM ARCs through modification of the PAA pH. An optimal trade-off is found at a PAA pH value of 5.2.

> and other optoelectronics<sup>8</sup> also utilize ARCs to maximize performance. ARCs also provide glare reduction in eyeglasses,9 digital displays,<sup>10</sup> and hand-held electronics. For a single-layer ARC, the maximum destructive interference for a specific reflected wavelength can be controlled by setting the optical thickness (product of refractive index and actual thickness) to one-quarter of the wavelength (OT =  $\lambda/4$ ). For complete destructive interference, the refractive index of the coating must equal to the square root of the product of the refractive indices for the media surrounding the coating  $(n_c = \sqrt{n_1 n_2})$ , which makes the amplitudes of the two reflected waves equal. For a typical application, the coating would be deposited onto a glass or polymer substrate ( $n_1 \cong 1.50$ ) and be immersed in a medium of air  $(n_2 = 1.00)$ . In that circumstance, an optimal refractive index of the coating would be  $n_c = 1.22$ . The refractive index is intrinsic to the specific coating material used, and therefore it is not easily altered other than changes to material porosity.<sup>11</sup> ARCs are traditionally composed of MgF2, which is wellknown to have peak transmittances less than 98%,12-14 due to its non-ideal refractive index ( $n \approx 1.38$ ). Other than PECVD, methods such as RF magnetron sputtering,<sup>1</sup> spin coating,<sup>2</sup> sol-gel synthesis,<sup>3</sup> focused ion beam (FIB),<sup>6,7</sup> and nanolithography<sup>8</sup> are widely used methods to produce ARCs. Unfortunately, these production techniques generally produce a single homogeneous



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<sup>&</sup>lt;sup>a</sup> Department of Materials Science and Engineering, Virginia Tech, Blacksburg, Virginia 24061, USA. E-mail: metzmanj@vt.edu

<sup>&</sup>lt;sup>b</sup> Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, USA

E-mail: rheflin@vt.edu

<sup>&</sup>lt;sup>d</sup> Division of Nanoscience, Virginia Tech, Blacksburg, Virginia 24061, USA

<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: PAH/PAA optical constants, PAH/PAA multilayer growth thickness/roughness, exponential growth constants of PAH/PAA multilayers, interlayer ISAM ARCs various thicknesses, extensive SEM imaging, and further tribology measurements. See DOI: 10.1039/ c7tc04457g

material with a refractive index far from the ideal value.<sup>15</sup> Additionally, their cost and/or scalability remain as definite constraints for large-areas and complex surfaces.

Ionic self-assembled multilayers (ISAMs), also known as layer-by-layer (LbL) films or polyelectrolyte multilayers (PEMs), are an attractive route to ARC production, given their inexpensive and simple yet versatile nature. The well-studied process is based on immersing a charged substrate in alternating polycation and polyanion solutions to grow a film primarily through electrostatic attraction. A single ISAM film can easily be composed of a multitude of materials deposited homogenously onto flat or curved surfaces. The deposition of a single layer is completed when a charged material has overcompensated the opposite charge of the previous layer. The technique was founded by Iler<sup>16</sup> and later revitalized by Decher.<sup>17</sup> Previously, we used the ISAM fabrication method to construct ARCs with poly(allylamine hydrochloride) (PAH) and silica nanoparticles (SiO<sub>2</sub> NPs).<sup>18</sup> The random closed-packed (RCP) self-assembled structure of the 45 nm SiO<sub>2</sub> NPs forms a porosity of 36% and an average refractive index (combining the SiO<sub>2</sub> NPs and pores) between 1.25 and 1.34. The proximity of refractive indices to the ideal value allow for transmittance and reflectance to be greater than 98% and less than 0.2%, respectively, in the visible wavelength range. The porosity has a considerable advantage for shifting the refractive index for anti-reflection, but the films inherently lacked mechanical stability. Without mechanical stability, the excellent optical properties of the ARCs have little value.

The thermal crosslinking reaction of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) provides an effective means for stabilizing ISAM films after growth, without adverse substrate effects.<sup>19-29</sup> The cationic functional amine groups  $(-NH_3^+)$  of PAH and the anionic carboxylic acid functional groups (-COO<sup>-</sup>) of PAA form ionic complexes during growth of the ISAM films. The understanding of a multilayer film's structure is a necessary element in the interpretation of its mechanical and growth properties. Given the nature of PAH and PAA as weak polyelectrolytes, it's well-known that the degree of ionization, charge density, and resultant multilayer thickness are highly sensitive to pH variation.<sup>30,31</sup> The  $pK_a$ value, also known as the acid dissociation constant, is the pH at which the average ionization of the polyelectrolyte chains is 50%. Adjustment of a weak polyelectrolyte's pH near its  $pK_a$  can result in dramatic rises in layer thicknesses from 4 Å to 80 Å.<sup>30</sup> The PAA  $pK_a$  has been reported to be located in range of 5.5–6.5 while in solution and without the addition of salt.<sup>31</sup> As the pH nears the  $pK_a$  value from above, a high level of protonation occurs in the PAA polymer chains, which corresponds to large increases in PAA layer thickness. The rise in thickness is partially attributed to the layer roughness, as the chains lift up, with an increased population of polymer loops and tails, due to decreased intrachain repulsion. At pH values well above the PAA  $pK_a$ , PAA chains have a higher degree of ionization. This increased negative charge for the individual PAA chains results in fewer required chains for charge reversal of the previous layer and a lower bilayer thickness. It has been shown experimentally that PAA deposited into multilayer films containing highly charged weak polycations (such as PAH) results in a dramatic shift in the PAA degree of ionization.<sup>31,32</sup> That is, the  $pK_a$  of PAA in a PAH/PAA multilayer film shifted to approximately 2.2, which is vastly different from in solution or a single layer casted film.<sup>31</sup> This was further confirmed by immersing PAH/PAA multilayers (of a wide range of pH values) into acidic baths, which led to spinodal decomposition.<sup>32</sup> After film fabrication, stability of the films by crosslinking can be induced by means of a thermal treatment. The end result of the crosslinking procedure is a conversion of the amine and carboxylic acid groups to linkage amide bonds. Several techniques have been utilized to provide a comparison for the range of factors ultimately affecting the stability provided by this crosslinking process.

In general, scratch testing has also been well established for defining the wear resistance for thin films at both a micro<sup>24,25,27,33–37</sup> and macro-scale.<sup>28,37–41</sup> Generally, scratch testing is a purely comparative study, to be used for similar types of films, with quantitative values depending heavily on the testing conditions (geometries of the abrasive, calibrations, *etc.*).

Nanoindenters are standard for micro-scale scratch testing, as well other mechanical properties such as hardness and elastic modulus,<sup>21,28</sup> although the AFM has also been proven to be effective.<sup>24,25</sup> Scratching procedures on a nanoindenter can ultimately be used to determine specific critical loads where film failure occurs by plastic deformation, surface abrasion, or delamination of the film.<sup>27,33-35</sup> Yang *et al.*<sup>27</sup> have identified the mechanical properties for wear resistant PAH/PAA films by the load in which the film is "peeled away" or delaminated from the substrate by utilization of a microtriboindenter and a scratch tester. Scratch testing can additionally be used to compare scratch penetration depths for normal force applied to a film's surface,<sup>33,36,37</sup> a complementary characterization method to solely finding the critical loads.

Macro-scale scratch testing may lead to a more complete understanding of a film's scratch-resistance, as large areas of the films are subjected to abrasion. This type of measurement is inherently more simplistic than the micro-scale in methodology, as changes in films' properties are used as a metric after scratching, rather than critical loads of failure. This includes haze,37,38 reflectance,39,40 transmittance,41 and mass loss.41 Some facile macro-scale scratch testing methods involve pencil hardness testing<sup>38</sup> and the scotch tape peel test<sup>28,42</sup> for a qualitative film adhesion evaluation. The scratch-resistance of silica ARCs have been examined by the operation of a Taber<sup>®</sup> Abraser, a standardized instrument that utilizes weighted rotating abrading wheels to perform cyclical scratches on a sample.<sup>38,39</sup> Macroscopic scratch testing on ARCs have also been successfully accomplished through wiping by a motorized translational stage equipped with a weighted abrasive material<sup>37,40</sup> or by merely wiping samples manually with a laboratory cleaning tissue.<sup>41</sup>

In this report, we present a method for incorporating PAH and PAA polyelectrolyte interlayers with silica nanoparticles to form stably crosslinked, anti-reflection coatings with improved anti-scratch properties. The films' design was similar to the previous method used by our group,<sup>18</sup> but with an extra bilayer of PAA/PAH added between PAH and the SiO<sub>2</sub> NP's. To our

knowledge, this is the first report to apply the beneficial properties of pure PAH/PAA multilayers into composite films, including SiO<sub>2</sub> NP's, for ISAM ARCs. These additional polyelectrolytes provide additional mechanical stability to the film, especially after thermal crosslinking. Prior to incorporation into interlayer ISAM ARCs, the diffusive properties of PAA in PAH/ PAA multilayers (without SiO<sub>2</sub> NP's) were examined through a variation of polyelectrolyte pH. We applied those findings to interlayer ISAM ARCs, where the diffusion and thickness of PAA was discovered to drastically affect the films' properties. These dramatic changes were further understood with respect to the films' surface morphology, through field emission scanning electron microscopy (FESEM). We show the correlation between the crossover from linear to exponential-growth in PAH/PAA multilayers and the observable rise in scratch resistance of the interlayer ISAM ARCs. The essential goal for the study was an optimization of both the anti-reflection and scratch resistance in the thermally-crosslinked interlayer ISAM ARCs through the variation of the pH of PAA.

## 2. Experimental

#### 2.1 Materials

Poly(allylamine hydrochloride) ( $M_v = 120\,000-200\,000$ ) was purchased from Alfa Aesar. Poly(acrylic acid) ( $M_v = 450\,000$ ) was purchased from Sigma Aldrich. Silica nanoparticle (SNOWTEX ST-20L, 45 nm average particle diameter, 3.76 M) solution was purchased from Nissan Chemical. Hydrochloric acid (HCl, Certified ACS Plus) and Sodium Hydroxide (NaOH, Certified ACS, Pellets,  $\geq$  97.0%) were purchased from Fisher Scientific. The polyelectrolyte solutions and ISAM rinsing buffers used 18 MQ deionized (DI) water. Glass microscope slides were purchased from Fisher Scientific with 76.2  $\times$  25.4 mm dimensions. Polished silicon wafers of 4'' diameter, 500 micron thickness, and  $\langle 111 \rangle$ orientation were purchased from University Wafer. The wafers were cut to analogous microscope dimensions to be compatible with our programmable immersion machine. The same wafers were coated with 200 nm of Au and cut into  $1'' \times 1''$  squares to be used for FTIR.

#### 2.2 Instrumentation

A programmable immersion instrument from nanoStrata, Inc. was used to produce ISAM films. A Thermo Scientific Lindberg/ Blue M VO 914A-1 vacuum oven was used to thermally crosslink films. The laboratory house vacuum provided 20 inch Hg vacuum during crosslinking.

The transmittance and reflectance spectra were collected by a Filmetrics F10-RT-EXR spectrometer. The spectrometer wavelengths ranged from  $\lambda$  = 300 nm to 1700 nm.

Thicknesses above 20 nm and all rms roughness film values were measured with a Veeco DekTak 150 Stylus Profilometer, with a 2.5  $\mu$ m tip radius stylus and an application of 1 mg force. Several scratches were produced down to the substrate before crosslinking, using plastic tweezers. These scratches allowed for step thickness measurements on the films.

A J. A. Woollam VB-400 ellipsometer with a HS-190 monochromatic system was used to also measure thickness values, especially those less than 20 nm. All ellipsometry measurements were recorded from ISAM films deposited onto silicon substrates to increase the signal to noise. The ellipsometry measurements were recorded in a range of 400 to 1000 nm (with 5 nm increments), angles 55 to 75 degrees (by 10 degree increments), with 50 revolutions per measurement, and dynamic averaging. Initially, a bare silicon substrate was modeled and found to have a native oxide layer of 1.81 nm. A model was then built which involved three sections, a Cauchy layer, the silicon oxide layer, and the silicon substrate. The extinction coefficient was taken as zero for the entire measured spectrum, as the Cauchy layer assumed a transparent material. The Cauchy layer dispersion model for the film was represented by

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$
(1)

where *A*, *B*, and *C* are fit parameters, determined by the software. Several relatively thick films of ten to twenty PAH/PAA bilayers in the pH range of 4–6 were measured and analyzed by the modeling software. Thicker films were used to improve the accuracy of the model, due to the higher signal-to-noise ratio, when compared to thinner films. The model determined optical constants of A = 1.5373, B = 0.0053271, and C = 0 (not varied in the fit). The refractive index to wavelength relationship is represented in Fig. S1 in the ESI.† These optical constants were applied to the experimental polarization data for the rest of the films to determine the thickness. Mean squared error (MSE) values were consistently below 5, which signified that the data fit well to the model. All of the quantitative values reported above involved averaging three to five measurements per sample.

The micro-scale scratch test results were obtained with a Hysitron TriboIndenter, using a 1 µm radius conical diamond tip. The instrument's scanning probe microscope (SPM) scanned the scratched section in situ, directly after scratching. The scratch test procedure involved ramping of the normal force linearly from near absent force to a specified peak force, over a lateral distance of 10-20 µm. The peak force was varied from 50-300 µN based on the nature of the films, to effectively maximize the scratch's resolution. After the scratch, the in situ SPM was then applied to the 10–20  $\mu$ m<sup>2</sup> area, centered on the scratch. Typically, the beginning of the scratch was found by a defined decrease height profile in the in situ SPM image of the scratched film. The scratch's height profile was compared in the SPM image with the overall film roughness, to find a starting point for apparent abrasion of the film. This location was qualitatively cross-checked by the visual appearance of the scratch in the SPM image to confirm that the scratch was physical. The lateral location of the scratch was then correlated to the specific location's normal force, which was designated as the critical load value. The determination of this value is relative to the TriboIndenter setup parameters (tip geometry, tip size, calibration, etc.) and only serves as a method of comparison between interlayer ISAM ARCs of different growth or crosslinking conditions.

#### Paper

The macro-scale scratch test was performed by sliding the end of a stainless steel rod over the samples. The end of the rod had a circular profile of 1.29 cm<sup>2</sup>, and the total mass of the rod was 451 grams. The rod was fixed in the x-y plane and was free to move in the z-direction, by an open clamp attached to a shelf above. The end of the rod was wrapped tightly with three laboratory cleaning tissues (Kimberly-Clark<sup>™</sup> Professional Kimtech Science<sup>™</sup> Kimwipes<sup>™</sup> Delicate Task Wipers, 1-Ply) and attached with tape. New cleaning tissues were installed after each sample for consistency. The samples were secured to a motorized translational stage (MLS203, Thorlabs). Three single passes at approximately  $0.4 \text{ cm s}^{-1}$  were made down the length of the sample to cover the entire area of the film. Four samples were abraded from each sample set, corresponding to the PAA pH and whether the films were crosslinked or uncrosslinked. A haze meter (BYK Gardner) was used to measure the haze of each sample before and after the scratch, at three different spots per sample. The results were averaged for each sample set. The percent difference for each sample set was calculated by dividing the difference of the haze before and after the scratch by the haze before the scratch.

A LEO (Zeiss) 1550 FESEM with an accelerating voltage of 5 kV was used to scan interlayer ISAM ARCs. Fourier transform infrared spectroscopy measurements were acquired using a Bruker IFS 66v/S, type I18174. The unit collected spectra in reflectance mode using OPUS for 100 scans per spectrum at a scan speed of 20 kHz with a MIR-Source and a KBr beam splitter. Samples were pressurized at  $\sim$  24 mbar.

#### 2.3 Solution formation

The PAH and PAA solutions were formed by mixing the polymer powders into DI water at a concentration of 10 mM. The solutions were adjusted to a neutral pH value and then sonicated for 3 hours. The pH of the solutions was adjusted by the addition of 1.0 M HCl and 1.0 M NaOH solutions. A vacuum filtration assembly with 3.0  $\mu$ m filter was then used to remove large aggregates from the solution. This filtration method vastly improved film homogeneity and clarity. The SiO<sub>2</sub> NP solution's concentration was left unaltered at 20 wt%, but its pH value was adjusted to 9. The nomenclature here for a polyelectrolyte with a specific pH is denoted as PAA<sub>x</sub>, where PAA is the polyelectrolyte and *x* is the pH value.

#### 2.4 Substrate preparation

Organic contaminates were removed from glass microscope slides with the use of acetone and laboratory cleaning tissues. The slides were sprayed with laboratory  $N_2$  gas to remove any excess acetone and lint particles. The RCA cleaning method<sup>43</sup> was then used to vigorously clean the slides and functionalize the surfaces with hydroxyl groups (OH<sup>-</sup>). The slides were then rinsed thoroughly with DI water and dried under vacuum. This method provided a clean slide with an abundance of negative charges, ready for ISAM film growth.

#### 2.5 Interlayer film architecture and fabrication

The interlayer ISAM ARC architecture was designed to incorporate the anti-reflection effects from the porous silica nanoparticle



Fig. 1 Interlayer ISAM ARC architectural schematic.

matrix, while combining the mechanical stabilization effects of the crosslinking polymers. The order of the interlayer stack was PAH, PAA, PAH, and SiO<sub>2</sub> NPs layers. Completion of one repeat is denoted as a "quadlayer". The quadlayers are represented by  $[PAH_{7.0}/PAA_x/PAH_{7.0}/SiO_{2.9.0}]_y$ , where x and y correspond to the PAA pH and the number of quadlayers, respectively. The pH of only PAA was varied for this study. The pH of PAH and the SiO<sub>2</sub> NPs remained constant throughout the entire study at 7.0 (PAH<sub>7.0</sub>) and 9.0 (SiO<sub>2 9.0</sub>), respectively. This is consistent with the previous studies by our group.<sup>18</sup> All interlayer ISAM ARCs ended with a "sealant" stack that consisted of a single bilayer of PAH and PAA that was deposited on top to further promote the mechanical integrity of the film. Therefore, the variable y is denoted with the number of complete quadlayers plus 0.5. For instance, y = 4.5 means four quadlayers with an additional PAH/PAA bilayer. A pictorial representation of this architecture is shown in Fig. 1.

The programmable immersion instrument used to fabricate the ISAM films allowed for fine-tuned control over the specific fabrication conditions. This includes dipping time and substrate spinning speed. After an extensive period of experimentation with a wide range of fabrication conditions (not included in this paper), specific dipping conditions were established to maximize film homogeneity and reproducibility. The substrate was dipped into the polyelectrolyte (PAH, PAA, and then PAH again) solutions for five minutes each without any spinning. The substrate was dipped into the SiO<sub>2</sub> NP solution for fifteen minutes, while spinning at 3000 rpm. In between each solution, the substrates were rinsed by spinning at 3000 rpm in a neutral water buffer for 135 seconds. The programmable immersion machine contained eight dipping solutions, which conveniently translated to four monolayer dipping steps, each followed by one neutral deionized water rinse step.

## 3. Results and discussion

#### 3.1 PAH/PAA diffusion and exponential growth

From previous reports, exponential-growth in polyelectrolyte films has been repeatedly confirmed to fundamentally rely on uncompensated, free chain diffusion.<sup>44–50</sup> To verify this was true for PAH/PAA multilayers, the dependence of exponentialgrowth on the variation of the PAA pH was evaluated. The pH of PAH was maintained at a value of 7.0, identical to the conditions for the interlayer ISAM ARCs. PAH<sub>7.0</sub> is reported as approximately 80% and 92% ionized in solution and in a

multilayer film, respectively.<sup>31</sup> The PAH chains at this pH are interpenetrated with neighboring layers,<sup>30,48</sup> but are virtually absent of free diffusing chains. The PAH chains at this pH are flat and rigid,<sup>21,30,50</sup> with a tight conformation to the previous layer. The PAA pH was varied coarsely from PAA<sub>3.0</sub> to PAA<sub>6.0</sub> and finely from PAA<sub>5.0</sub> to PAA<sub>6.0</sub>, each with a set of one through five PAH/PAA bilayers for thickness and RMS surface roughness measurements (ESI,<sup> $\dagger$ </sup> Fig. S2). The range of PAA<sub>3.0</sub> to PAA<sub>6.0</sub>, represents an ionization range of 43% to 77%.<sup>31</sup> These ranges were specifically examined because they would lead to a fuller understanding of the properties of the interlayer ISAM ARCs, for which the PAA pH was varied in the same fashion. As presented in Fig. S2 (ESI<sup>†</sup>), from PAA<sub>6.0</sub> to PAA<sub>3.0</sub>, the PAH/ PAA multilayer growth shifts from linear to exponential-growth, respectively. The primary crossover from linear to exponentialgrowth occurs near PAA<sub>5.4</sub>. At PAA<sub>5.2</sub>, the exponential-growth becomes even more pronounced and continues to increase to PAA<sub>4.0</sub>. As the exponential-growth characteristics increase, the multilayers become more interpenetrated, but lose the high levels of ionic crosslinking.<sup>30,48</sup> From PAA<sub>5.2</sub> to PAA<sub>4.0</sub>, the overall shape of the exponential curves is nearly identical and the primary difference between them is the slope of the initial bilayers. The overall rise in the exponential slope with a decrease in the PAA pH confirms a reduction in the charge density of the PAA chains and an increase in the concentration of free, diffusing chains. At a higher number of bilayers (10-20) for the range of PAA<sub>5.0</sub> to PAA<sub>6.0</sub> (ESI,† Fig. S4), the growth eventually shifted to linear, previously theorized to occur when the film thickness exceeds the point of saturation in the concentration of free diffusing chains necessary for exponential-growth.44,47

#### 3.2 FTIR characterization of PAH/PAA multilayers

Despite variations of interpenetration and diffusion effects in PAH/PAA ISAM films at different values of pH of PAA, the ionic bonding between polyelectrolyte species is inherently nonrobust. Elevated temperatures in the range of 150-250 °C have been clearly shown as an effective method to induce stability through crosslinking in PAH/PAA films.<sup>19,21,25,27,28,49,51</sup> The crosslinking reaction results in covalent amide bond formation between the two functional groups of the polyelectrolytes. The confirmation of this reaction was investigated through Fourier transform infrared spectroscopy (FTIR) on four identical twobilayer PAH<sub>7 5</sub>/PAA<sub>4 5</sub> films that were grown onto gold-coated substrates. Based on reported  $pK_a$  values,<sup>31</sup> the polyelectrolytes have a degree of ionization greater than 50% at this pH, suggesting that the acquired spectra would provide significant intensity for the ionized and unionized species. The films were thermally treated at 75, 150, 200, and 250 °C for one hour to systematically establish a trend between temperature and crosslinking, represented in Fig. 2.

In the 75 and 150 °C films, prominent peaks at 1560 and 1403 cm<sup>-1</sup> are assigned to the carboxylate ( $-COO^-$ ) asymmetric and symmetric stretching, corresponding to the ionized (unprotonated) portions of the PAA polyelectrolyte. The peak located at 1720 cm<sup>-1</sup> is assigned to the carboxyl absorption of the carboxylic acid (-COOH) groups, characteristic of the



Fig. 2 FTIR spectra for two-bilayer PAH<sub>7.5</sub>/PAA<sub>4.5</sub> films on Au substrates.

unionized (protonated) PAA polyelectrolyte segments.<sup>19,26,29,31,49</sup> In the 200 °C film, the relative protonated -COOH peak intensity decreased and shifted from 1720 cm<sup>-1</sup> to 1733 cm<sup>-1</sup>. This is typical for amide formation and indicates a change of the hydrogen bonding.19,23,26 The unprotonated -COO- peaks at 1560 cm<sup>-1</sup> and 1403 cm<sup>-1</sup> completely disappeared from the 200 °C film spectrum, and were replaced by peaks at 1660  $\text{cm}^{-1}$ and 1535 cm<sup>-1</sup> that represent amide I and amide II peaks, respectively.<sup>19,23,26,29</sup> The amide I peak is assigned to the primary and secondary vibrations that corresponded to the carbonyl (C=O) stretch (70-85%) and the amide (C-N) stretch (10-20%), respectively. Similarly, the amide II is peak also composed of primary and secondary vibrations, which correspond to the amino (N-H) bending (40-60%) and the amide (C-N) stretch (18-40%).<sup>52</sup> These results provide confirmation of the covalent amide bond formation by thermal crosslinking between the two polyelectrolytes at this specific temperature and pH range.

The 250 °C film showed the same general features as the 200 °C film, although the amide peaks are far weaker. We suspect that at this temperature, the decomposition process of the polyelectrolyte film has begun. This may be specific to the film formation conditions used here, given that other reports show that this temperature is suitable for crosslinking and amide formation.<sup>26,27</sup>

#### 3.3 Interlayer UV-vis-IR spectra

It is well established that polyelectrolyte multilayer assemblies are not structured as uniform lattices, but rather initiate as isolated grains/islands due to material charge repulsion.<sup>45–47</sup> In the particular case of PAH/SiO<sub>2</sub> NP multilayer films, the SiO<sub>2</sub> NP islands are encapsulated by stiff and extended PAH polyelectrolyte chains until the achievement of charge overcompensation. At this point in the growth process, further PAH chains in the solution are electrostatically repelled and eventually a rinsing stage would remove any weakly bound chains. The approximate PAH encapsulation thickness for the highly charged state is less than 0.5 nm. When the film is immersed into the SiO<sub>2</sub> NP solution again, the NPs are attracted toward the PAH-encapsulated islands to eventually develop a contiguous RCP structure. As described above, the porosity within that structure is crucial in order to maintain the ideal refractive index for anti-reflection.

The porosity remains vital to the interlayer ISAM ARCs described here, especially as two polyelectrolytes are added into the composition of the film. Given that the refractive indices of the polyelectrolyte and SiO<sub>2</sub> NPs are comparable  $(n \approx 1.5)$ , a NP coating with smaller polyelectrolyte thickness provides a high level of porosity and a low average refractive index. On the other hand, a larger polyelectrolyte thickness will increase the overall average refractive index due to the decreased porosity as some of the void space is filled by polyelectrolyte. However, this would also allow for a greater range of diffusion of PAA and result in a more interpenetrated SiO<sub>2</sub> NP encapsulation. Our hypothesis was that a thicker and more interpenetrated polymer matrix would provide higher levels of cohesion and crosslinking sites to strengthen the mechanical integrity of the film. As mentioned previously, the sole experimental variable considered was the pH of PAA within the interlayer films in order to control the polyelectrolyte thickness and interpenetration to examine the effect on the void space of the film. This variable was demonstrated above as the factor that determines the PAA charge density, the concentration of free diffusing PAA chains, and the film thickness for films consisting only of polyelectrolyte.

The optical destructive interference in the reflected light normal to the film's surface yields defined interference fringes

and provides the anti-reflection properties. The wavelength maxima for destructive interference are proportional to the thickness of the nanoparticle-containing films. The film thickness is a simple parameter to adjust, due to its proportionality to the number of deposited layers. In this study, we focus on a set of films with an identical number of layers that yields the first anti-reflection peak in the visible wavelength range. Through preliminary studies, an interlayer film of four quadlayers or  $[PAH_{7,0}/PAA_x/PAH_{7,0}/SiO_{2,9,0}]_{n=4,5}$  (PAA as the last layer) is found to satisfy that condition. The spectra for the films composed of 1 to 3 quadlayers (with antireflection peaks in or close to the ultraviolet) are shown in Fig. S5 of the ESI.† To examine the coarse effects in films with PAA near to and far from the  $pK_a$ , we varied the pH from PAA<sub>3.0</sub> to PAA<sub>6.0</sub> (incremented by 1.0). All of the films were thermally crosslinked at 200 °C for two hours. Fig. 3a-e shows the measured values for the transmission, reflection, absorbance due to scattering  $(A_s)$ , thickness, and RMS surface roughness as a function of the PAA pH. The transmission and reflection spectra are also compared to those of bare glass.

At PAA<sub>6.0</sub>, the pH was far from the  $pK_a$ , which leads to highly charged individual chains and the concentration of free, uncompensated chains is low. Therefore, the overall resultant polyelectrolyte thickness is low, as the chains tightly encapsulate the SiO<sub>2</sub> NPs. This allows the desired porosity and refractive index of the films, as shown in high levels of anti-reflection. This structural arrangement yields the maximum transmission and minimum transmission levels of 99.08% and 0.04%, respectively, as seen in Fig. 3a and Table 1. It is found that thermal



**Fig. 3** Measurements of (a) transmittance, (b) reflectance, (c) absorbance due to scattering ( $A_s$ ), (d) thickness, and (e) RMS surface roughness for 4-quadlayer interlayer ISAM ARCs of the architecture [PAH<sub>7</sub>/PAA<sub>x</sub>/PAH<sub>7</sub>/SiO<sub>2</sub> 9]<sub>*n*=4.5</sub> with *x* varied from 3.0 to 6.0 with increments of 1.0. All of the films were thermally crosslinked at 200 °C for 2 hours.

Table 1 Optical and physical properties for 4-quadlayer [PAH<sub>7</sub>/PAA<sub>x</sub>/PAH<sub>7</sub>/SiO<sub>29</sub>]<sub>n=4.5</sub> films

Pap	er
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Interlayer PAA pH	Transmittance maxima (%)	Reflectance minima (%)	Absorbance slope	Thickness (nm)	RMS roughness (nm)
Glass	92.40	7.72	_	_	_
3.0	93.49	0.52	$9.64 imes10^8$	146.05	73.22
4.0	96.37	0.07	$6.56 imes10^8$	136.35	11.05
5.0	96.84	1.11	$4.73 imes10^8$	141.07	5.03
5.2	98.81	0.14	$5.35 imes10^8$	151.59	5.75
5.4	98.76	0.04	$4.27 imes10^8$	148.05	4.64
5.6	98.80	0.13	$4.59\times 10^8$	143.78	5.06
5.8	99.18	0.30	$1.51 imes 10^8$	124.14	5.15
6.0	99.08	0.04	$5.06 imes10^8$	127.90	5.17

crosslinking actually increases anti-reflection properties for this set of films, most likely attributed to decreased surface roughness.<sup>27</sup> In the interlayer ISAM ARCs that contain PAA<sub>5.0</sub>, the peak transmittance reduces to <97%. As the PAA pH in the interlayer ISAM ARC was altered below the solution  $pK_a$ , the transmittance was reduced nearly to that of glass. The reflection minima of PAA<sub>3.0</sub> and PAA<sub>4.0</sub> in Fig. 3b also blue-shift into the UV range as a result of large degrees of optical scattering, as discussed below. The absorbance due to scattering ( $A_s$ ) was calculated according to

$$A_{\rm s}(\lambda) = -\log\left(\frac{T(\lambda)}{1 - R(\lambda)}\right) \tag{2}$$

where *T* is the transmission percentage and *R* is the reflectance percentage at a specific wavelength.  $A_s$  is proportional to the scattering cross-section through:

$$A_{\rm s}(\lambda) = C l \sigma_{\rm s}(\lambda) \tag{3}$$

where *C* is the concentration, *l* is the path length, and  $\sigma_s$  is the scattering cross-section, which is proportional to  $(\lambda)^{-4}$  in the case of Rayleigh scattering.

Given the non-absorbing nature for the constituents within the interlayer ISAM ARCs in the wavelength range considered, the loss is assumed to be completely due to optical scattering. The absorbance due to scattering, shown in Fig. 3c, displays a linear dependence on the inverse wavelength to the fourth power ( $\lambda^{-4}$ ), characteristic of Rayleigh scattering. As the pH of PAA is decreased towards its  $pK_a$ , there are strong increases in surface roughness and optical scattering. This is quite apparent in the comparison of the PAA<sub>3.0</sub> and the PAA<sub>6.0</sub> films' A<sub>s</sub> slope at  $9.64 \times 10^8$  and  $5.06 \times 10^8$ , respectively. The separation by almost a factor of 2 in the scattering loss between the two pH extremes exemplifies the dramatic change in structure of the polyelectrolyte encapsulation within the interlayer films. The correlation between interfacial surface roughness and optical scattering loss has been widely established.53,54 It should also be noted that while the reflectance approaches its minimum at wavelengths shorter than 400 nm for the pH 3.0 and 4.0 cases, the transmittance maximum appears to be shifted into the visible for these two cases. This is because of the strong scattering in the UV, which decreases the transmittance in this wavelength region and masks where the transmittance peak would otherwise occur.

The total film thickness in the range of  $PAA_{3.0}$  to  $PAA_{6.0}$  in Fig. 3d illustrates that a change in PAA pH did not have a

significant effect on the overall thickness of the films. Based on previous studies done on interlayers of PEI/PAA/PEI/Na+montmorillonite (MTM),<sup>55</sup> we are confident that the SiO<sub>2</sub> matrix should not completely block polyelectrolyte diffusion during growth. Exponential-growth was not directly seen in these thickness measurements since the bulk of the film thickness is determined by the diameter of the SiO<sub>2</sub> NPs and increased thickness of the polyelectrolytes mostly fills in the void space between the NPs. However, the dramatic increased thickness of the PAH/PAA encapsulating films is seen clearly in the FESEM results shown below.

As discussed in a later section, an adjustment from PAA<sub>6.0</sub> to PAA<sub>5.0</sub> in the interlayer ISAM ARCs increases the abrasion resistance quite significantly. In terms of the optical properties, the former has excellent anti-reflection where the latter is significantly worse. Because of the large variation in optical and mechanical properties for a 1.0 increment in pH, we focus on the pH values in the range of PAA<sub>5.0</sub> to PAA<sub>6.0</sub>, with increments of 0.2 pH units. The transmittance, reflectance,  $A_s$ , thickness, and RMS surface roughness were recorded after drying and thermally crosslinking the films (Fig. 4a–e). The key parameters for the 4-quadlayer interlayer ISAM ARCs are presented in Table 1. For 1 to 3-quadlayer films in the range of PAA<sub>5.0</sub> to PAA<sub>6.0</sub>, results can be found in Fig. S6 of the ESI.<sup>†</sup>

The differences between transmittance and reflectance spectra for interlayer ISAM ARCs in the range of  $PAA_{6.0}$  to  $PAA_{5.2}$  are quite small. The percent decrease in peak transmittance (Fig. 4a) of the  $PAA_{6.0}$  to  $PAA_{5.2}$  was 0.27% compared to 2.24% for  $PAA_{6.0}$ to  $PAA_{5.0}$ . The increase in the reflectance minimum (Fig. 4b) of  $PAA_{6.0}$  to  $PAA_{5.2}$  is only 0.10%. The substantial differences in a 0.2 incremental variation from  $PAA_{5.2}$  to  $PAA_{5.0}$ , however, highlight this range as the critical point where the films lose their excellent anti-reflection, but acquire a considerable rise in mechanical robustness (as shown later).

The  $A_s$  slope only changes modestly in the alteration of PAA<sub>6.0</sub> to PAA<sub>5.0</sub> in the interlayer ISAM ARCs. as shown in Fig. 4c and Table 2. The significant decrease in peak transmittance in the interlayer ISAM ARC with PAA<sub>5.0</sub> is primarily due to increased reflectance (due to an increase in the refractive index of the film) rather than increased scattering loss. The small ARC thickness variation in Fig. 4d is again because the SiO<sub>2</sub> NPs dominate the overall thickness of the films. The RMS surface roughness values in Fig. 4e also show little variation in this pH range of PAA.



**Fig. 4** Measurements of (a) transmittance, (b) reflectance, (c) absorbance due to scattering ( $A_s$ ), (d) thickness, and (e) RMS surface roughness for 4-quadlayer interlayer ISAM ARC's of the architecture [PAH<sub>7</sub>/PAA<sub>x</sub>/PAH<sub>7</sub>/SiO<sub>29</sub>]<sub>n=4.5</sub> with x varied from 5.0 to 6.0 by 0.2 increments. All of the films were thermally crosslinked at 200 °C for 2 hours.

**Table 2** Thermal crosslinking conditions (maximum temperature and dwell time) to the critical load ( $L_{c1}$ ) for (PAH<sub>7</sub>/PAA<sub>7</sub>)<sub>10</sub>-(PAH<sub>7</sub>/PAA<sub>7</sub>/PAH<sub>7</sub>/ SiO<sub>9</sub>)<sub>4</sub>-(PAH<sub>7</sub>/PAA<sub>7</sub>)<sub>10</sub> interlayer ISAM ARCs. Note that this interlayer architecture is different from that used elsewhere in this paper

	$L_{c1}$ ( $\mu N$ )		
Duration (h)	180 °C	200 °C	
1	13.34	22.46	
2	22.75	41.23	
10	17.23	34.38	
24	—	22.38	

#### 3.4 Interlayer FESEM characterization

The inspection of the interlayer ISAM ARCs surface morphology at the nanoscale provides a deeper understanding of the optical spectra and roughness characteristics. After the previous measurements were made, the interlayer ISAM ARCs of 4-quadlayers in the pH range of  $PAA_{3.0}$  to  $PAA_{6.0}$  were prepared for electron microscopy (Fig. 5a–d).

In Fig. 5d for  $PAA_{6.0}$ , the surface looks nearly identical to  $PAH/SiO_2$  NP films created previously by our group.<sup>18</sup> The encapsulating polyelectrolytes are so thin due to their tightly-bound, highly-charged nature that they are not visible, and the RCP structured SiO<sub>2</sub> NPs dominate the composition of the film. As this film exhibits excellent anti-reflection, the corresponding structure and void fraction of the SiO<sub>2</sub> NP network provides a refractive index close to the ideal value of 1.22. Furthermore, the homogeneity of the SiO<sub>2</sub> NPs structure and the lack of



**Fig. 5** FESEM characterization at 200k× magnification for 4-quadlayer interlayer ISAM ARC's of the architecture  $[PAH_7/PAA_x/PAH_7/SiO_{2.9}]_{n=4.5,r}$  where *x* was varied from (a–d) 3.0, 4.0, 5.0, and 6.0, respectively. All films were thermally crosslinked at 200 °C for two hours.

aggregation correlate with the low roughness values and minimal optical scattering for this film. While the  $SiO_2$  NPs network is contiguous in the 4-quadlayer interlayer ISAM ARCs for the PAA<sub>6.0</sub>, examination of the first quadlayers (ESI,† Fig. S7) show small island formations, characteristic of ISAM growth.

For interlayer ISAM ARCs with PAA<sub>5.0</sub>, shown in Fig. 5c, the observed morphology is fairly similar to that for PAA at pH 6.0, but an increase in the encapsulating polyelectrolyte thickness begins to be observable. This is most noticeable for the visible

layers below the surface. This suggests that free, uncompensated chain diffusion exists within the SiO<sub>2</sub> NP matrix, resulting in increased polyelectrolyte thickness. This larger polyelectrolyte thickness can be distinguished by a slight globular background, as opposed to the distinct spherical SiO<sub>2</sub> NP features. It can also be observed in the presence of a few polyelectrolyte branches that connect some encapsulated NPs. The increased polyelectrolyte thickness does not increase the overall film thickness, but it results in filling some of the void space, which leads to an increase in the refractive index as well as the surface roughness and optical scattering.

These effects become even more prominent in the interlayer ISAM ARC with PAA<sub>4.0</sub>, shown in Fig. 5b. Due to more free chains, the polyelectrolyte thickness increases more substantially and the number of polyelectrolyte branches have become noticeably accentuated. As shown below, this polyelectrolyte structure provides a continuous infrastructure that produces higher mechanical stability, especially after thermal crosslinking. Significant clustering of the SiO<sub>2</sub> NPs also develops. This clustering is attributed in part to the increased population of extended loops and tail segments in the PAA with higher levels of protonation, which also leads to larger surface roughness (Fig. 3e). This surface roughness and clustering contribute to increased optical scattering. Similar nanoparticle clustering by polyelectrolyte pH variation in films fabricated for a different application was previously shown in PEI/Au NPs films in order to control plasmonic interparticle spacing.<sup>56</sup>

At the end of the pH range with PAA<sub>3.0</sub> in Fig. 5a, the resultant surface morphology is quite striking. With the pH of the PAA below the value of the  $pK_a$  in solution, the polyelectrolyte is observed as a web-like network that strongly connects the SiO<sub>2</sub> NPs. This formation explains the very large optical scattering values and surface roughness shown in Fig. 3c and e. Microporous formations are reported extensively in the literature for acidic polyanion solution conditions, immersion into acidic buffers, or high salt concentrations in solution.<sup>20,22,32,49,57</sup> The previous reports show complete coverage of the entire area of film by the microporous formations and the structures have been commonly referred to as a "vermiculate morphology". In our case, the formations only partially cover the film surface area (ESI,† Fig. S8). To our knowledge, there are no cases in the literature that combine the microporous formation with nanoparticles. As seen in Fig. 5a, the SiO<sub>2</sub> NPs are primarily positioned on the outer edges of microporous formation, while very few are inside the structure. Since these microporous formations composed a relatively larger percent of the film, thermal crosslinking provides high levels of mechanical stability to the film, as shown in the next section. However, the fraction of void space in the film is greatly reduced, leading to an increase in the effective refractive index of the film and a corresponding large decrease in the anti-reflection properties of the film and the peak transmittance.

#### 3.5 Microscopic scratch testing

The TriboIndenter was used to study the scratch resistance at the micro-scale, which is related to the bulk cohesive (or interfacial toughness) properties for the interlayer films. The critical load due to abrasion  $(L_{c1})$  is the primary parameter used for the comparison of the films. The determination of this load requires a combination of qualitative and quantitative analysis through a visual inspection of the SPM image and the corresponding scratch height profile. Preceding the first location of abrasion, a region of plastic deformation commonly existed at lower normal forces. We designated the initiation of the scratch and the  $L_{c1}$  directly after this region, once abrasion was visually obvious. For a complementary measure of the scratch resistance in the films, the ratio of normal force divided by scratch penetration depth  $(L/P_d)$  was calculated for the interlayer ISAM ARCs. This ratio was calculated for the entire length of the scratch, starting at the scratch initiation. The  $P_{\rm d}$ was determined as the difference between the average height of the non-scratched area and height of a finite section, after the initiation of the scratch. In contrast to the  $L_{c1}$ , the critical load due to delamination  $(L_{c2})$  is more difficult determine and less informative for our films. Along with  $L_{c2}$  adhesive properties, the use of nanoindentation to acquire hardness and Young's modulus are also not reported for this particular study, due to the lack of correlation to the film growth conditions. Generally, nanoindentation is more challenging on films with larger porosities and smaller thicknesses, such as the interlayer ISAM ARCs. Since the thicknesses of these films are dominated by the SiO<sub>2</sub> NP's, the nanoindentation results for these particular films are inconclusive. As large-scale abrasion would ultimately lead to degradation of the anti-reflective properties in the interlayer ISAM ARCs, the  $L_{c1}$  and  $L/P_d$  were focused on for this assessment of micro-scale scratch testing.

Since thermal crosslinking was the primary mode for inducing mechanical stability after interlayer ISAM ARC growth, the crosslinking conditions were systematically assessed. These parameters were investigated in the initial exploration stages for this study, when the interlayer ISAM ARC architecture was somewhat different. The set of films tested contained ten-bilayer stacks of PAH/PAA before and after the quadlayer interlayers and the polyelectrolyte pH was fixed at 7.0. The abbreviated design for 4-quadlayers is as follows: (PAH7/PAA7)10-(PAH7/PAA7/PAH7/  $SiO_9)_4$ -(PAH<sub>7</sub>/PAA<sub>7</sub>)<sub>10</sub>. Due to the large number of polyelectrolyte layers, these films have poor anti-reflection, as the overall refractive index is far from ideal. However, after qualitative testing (rubbing with a cleaning tissue), the films show good mechanical stability against abrasion after thermal crosslinking. Therefore, the film set was used to develop a relationship of mechanical stability to the maximum temperature and the dwell time for thermal crosslinking. The maximum temperatures of 180 °C and 200 °C and dwell times of 1, 2, and 10 hours were tested (Table 2).

As shown in Table 2, the optimum thermal crosslinking conditions to maximize mechanical stability are 200 °C for 2 hours (under 20 inch Hg vacuum). The SPM image and scratch profile for a scratch done on this film is shown in Fig. 6e and f. An increase of the maximum temperature from 180 °C to 200 °C for nearly all of the dwell times produces a rise in the  $L_{c1}$  by approximately a factor of 2. Since the heating and cooling rate is set to 1 °C min<sup>-1</sup>, it should be noted that the 200 °C maximum temperature films are actually heated for

approximately 40 minutes more than the 180  $^{\circ}$ C films. When the heating and cooling ramp becomes less significant for the 10 hour dwell time, it is clearly shown that a maximum temperature of 200  $^{\circ}$ C resulted in an increase of mechanical stability. From these measurements, one can conclude that the 1 hour dwell time is inadequate for crosslinking. On the other hand, film degradation occurred for a dwell time of 10 hours and higher, which leads to the decrease in the mechanical stability. The maximum temperature of 220  $^{\circ}$ C is not tested for this preliminary study, although it was shown previously in the FTIR section that this temperature may lead to film degradation as well.

The optimal crosslinking conditions of 2 hours at 200 °C were then applied to the all of the subsequent interlayer ISAM ARCs of the architecture (PAH/PAA/PAH/SiO<sub>2</sub>)<sub>n</sub>. We performed mechanical stability testing on films of 4-quadlayers (n = 4.5) and for the PAA pH range of 3.0 to 6.0. Examples of the SPM image of the scratched area, normal force, and the height profile of the scratch for PAA<sub>3.0</sub>, PAA<sub>6.0</sub>, and one of the initial samples from Table 2 are shown in Fig. 6a–f.

For comparison, a 10-bilayer PAH<sub>7.0</sub>/PAA<sub>7.0</sub> ISAM film (no SiO<sub>2</sub> NPs) was also thermally crosslinked at the same conditions and tested by the TriboIndenter. The film was scratched with similar parameters used for the interlayer ISAM ARCs, and then imaged by *in situ* SPM directly after (ESI,<sup>†</sup> Fig. S9). That film has a significantly larger critical load than any of the films containing SiO<sub>2</sub> NPs. The transmittance maxima and the critical force are shown in Table 3 for the full set of values of the pH of PAH as well as for the PAH/PAA film.

The features and scratched section for the interlayer ISAM ARC with PAA<sub>3.0</sub> are similar to those found on the film with PAA<sub>4.0</sub> (not shown). As the same 1  $\mu$ m conical tip is used for scratching and SPM imaging, it must be noted that the images do not have high resolution that would show the features in Fig. 5a. For both of these two films, the scratch tip moves across the sample with increasing force, until it punctures the sample at the *L*<sub>c1</sub>. In the scratch profile of Fig. 6b, the tip puncture appears to reach the film's substrate, and subsequently rises back up to a lesser depth height for the majority of the scratch. The apparent "pile-up" pads on either side of the scratch seen in Fig. 6a can be explained by an excavation of thicker polymer layers within the film.

The interlayer ISAM ARCs with PAA3.0 and PAA4.0 possess much larger  $L_{c1}$  and  $L/P_d$  compared to the films with PAA adjusted to a higher pH ( $\geq$  5.0). The lower PAA pH films contain larger polyelectrolyte thicknesses and more interpenetrated PAH layers, which provides increased interfacial connectivity and scratch resistance. The interlayer ISAM ARC with PAA<sub>3.0</sub> has more than a factor of 2 larger  $L_{c1}$  than the PAA<sub>5.0</sub> case, for example. The variation of the  $L/P_d$  was not quite as dramatic, but still showed the same trends. For the lower PAA pH films, abrasion of the films by rubbing with a laboratory cleaning tissue proved to be difficult, providing qualitative evidence of the heightened scratch resistance for these films. It should also be noted that the  $L_{c1}$  for the interlayer ISAM ARC with PAA<sub>3.0</sub> approaches that of the 10-bilayer PAH7/PAA7 film. The scratch resistance progressively decreases with an increase in the PAA pH for the interlayer ISAM ARCs. For the interlayer ISAM ARCs



**Fig. 6** In situ SPM image, ramped normal force, and height profile of scratched area for 4-quadlayer interlayer ISAM ARC's of the architecture  $[PAH_{7/}PAA_x/PAH_7/SiO_{2g}]_{n=4.5}$ , with (a and b) PAA<sub>3.0</sub> and (c and d) PAA<sub>6.0</sub>. Interlayer ISAM ARC of (e and f)  $(PAH_{7.0}/PAA_{7.0})_{10} - (PAH_{7.0}/PAH_{7.0}/PAH_{7.0}/PAH_{7.0}/PAH_{7.0}/PAH_{7.0}/PAH_{7.0}/PAH_{7.0})_{10}$  also shown. All scratches were formed from the bottom-up in the SPM images (a, c and e) and shown left-to-right in normal force and scratch profiles (b, d and f).

**Table 3** Transmittance maxima and critical load for 4-quadlayer interlayer ISAM ARC's of the architecture  $[PAH_7/PAA_x/PAH_7/SiO_{29}]_{n=4.5}$ . A PAH<sub>7.0</sub>/PAA<sub>7.0</sub> ISAM film was included for critical load comparison

Interlayer PAA pH	3.0	4.0	5.0	5.2	5.4	5.6	5.8	6.0	10-Bilayer PAH/PAA
Transmittance maxima (%)	93.5	96.4	96.8	98.8	98.8	98.8	99.2	99.1	N/A
$L_{c1}$ (µN)	126	88.0	54.5	35.7	19.8	9.37	8.45	5.39	171.2
$L/P_d$ (µN nm <sup>-1</sup> )	7550	7420	5910	4910	3410	2570	2000	1600	—

with PAA<sub>5.0</sub> to PAA<sub>5.6</sub>, each increase of the pH by an increment of 0.2 leads to a drop in the  $L_{c1}$  by approximately a factor of 2.

#### 3.6 Macroscopic scratch testing

While the TriboIndenter is an excellent method for pinpointing film failure on a micro-scale, a thorough macro-scale characterization is also necessary to develop fuller representation of the interlayer ISAM ARCs resistance to abrasion. The weight from the stainless steel rod, along with laboratory cleaning tissues used as the abrasive material in the scratching, simulated heavy cleaning of the films (by rubbing) in a commercial environment. In order to quantify the degree of scratch resistance for each film set, the respective film's haze was measured. Haze is the percentage of diffuse luminous transmittance to total luminous transmittance, in relation to wide angle scattering (light scattered at angles greater than 2.5°).58 With the operation of a haze meter, haze can be easily measured before and after scratching. An increase in haze is directly related to scratching on the film because haze is dependent on light scattering, and light scattering is augmented with film roughness.<sup>53,54</sup> Previous reports have also used macro-scale scratching testing with a change in haze to define the level of scratch resistance for a film.<sup>37,38</sup>

For a complete comparison of the scratch resistance in interlayer ISAM ARCs, both uncrosslinked and crosslinked films were scratched with the previous range of PAA pH values, as shown in Table 4. For each PAA pH, the percent difference was calculated as ratio of the numerical difference of the haze before and after scratching, divided by the haze after scratching. The percent difference provided a more appropriate method for comparison of the scratch resistance across the PAA pH range and is graphically shown in Fig. 7.

These results show the clear improvement in the scratch resistance after thermal crosslinking of the interlayer ISAM

ARCs and the increased stability by the formation of amide bonds between the polyelectrolytes. Similar to the TriboIndenter results, the change in haze after scratching for PAA<sub>3.0</sub> and PAA<sub>4.0</sub> is very minimal, representing superior scratch resistance at these PAA pH's. This is true for the uncrosslinked films as well, implicating that simply an increase of polyelectrolyte thickness and interpenetration within the SiO<sub>2</sub> NP matrix will boost the scratch resistance, even without amide bond formation. However, as these films possess a lower PAA pH, they also have much higher levels of haze before scratching, which directly correlates to the higher absorbance due to scattering  $(A_s)$  values shown earlier. These very high levels of haze are unacceptable for use as ARCs. The crosslinking of the interlayer ISAM ARCs results in a reduction of the haze before scratching, throughout most of the tested PAA pH range. This confirms that thermal crosslinking reduces the film roughness, which in turn decreases the level of haze.27

For both uncrosslinked and crosslinked films, with increased PAA pH, the change in haze after scratching rapidly escalates, until reaching a plateau above pH 5.4. Thus, above  $PAA_{5.4}$ , the scratch resistance between different PAA pH's is comparable in interlayer ISAM ARCs.  $PAA_{5.4}$  also signifies the crossover from exponential and linear-growth relations in the PAH/PAA multilayer films. With a change from exponential to linear-growth, there is a resultant reduction in the polyelectrolyte thickness due to higher charge densities and less free chain diffusion. At these pH values of PAA, the PAH interpenetration diminishes and the SiO<sub>2</sub> NPs became less interconnected, which facilitates an ease of abrasion. For PAA pH at or above 5.2, the haze values drop below 0.5, which leads to increased levels of optical transmission.

The interlayer ISAM ARC optical properties and scratch resistance, shown together as transmittance and haze in Tables 3 and 4, respectively, hold an inverse relationship throughout the data.

 Table 4
 Haze measurements before scratching, after scratching, and the respective percent differences for 4-quadlayer interlayer ISAM ARC's of the architecture  $[PAH_7/PAA_x/PAH_7/SiO_{29}]_{n=4.5}$ 

	Uncrosslinked ARCs			Crosslinked ARCs (200 °C 2 hours)			
Interlayer PAA pH	Haze (%) before scratch	Haze (%) after scratch	% difference	Haze (%) before scratch	Haze (%) after scratch	% difference	
PAA 3.0	$25.40 \pm 2.2$	$27.35 \pm 1.5$	8	$23.15\pm2.5$	$23.35 \pm 1.8$	1	
PAA 4.0	$5.62\pm0.09$	$6.12 \pm 1.1$	9	$5.56\pm0.3$	$5.70\pm0.3$	3	
PAA 5.0	$0.86 \pm 0.05$	$1.40 \pm 0.2$	62	$0.78\pm0.1$	$0.93\pm0.05$	19	
PAA 5.2	$0.44\pm0.03$	$1.14\pm0.2$	158	$0.37\pm0.01$	$0.58\pm0.06$	56	
PAA 5.4	$0.53\pm0.08$	$1.37\pm0.2$	161	$0.44 \pm 0.08$	$0.87\pm0.2$	96	
PAA 5.6	$0.35\pm0.04$	$0.99\pm0.04$	183	$0.38\pm0.05$	$0.83 \pm 0.04$	115	
PAA 5.8	$0.42\pm0.06$	$1.13 \pm 0.07$	169	$0.39\pm0.05$	$0.95\pm0.02$	141	
PAA 6.0	$0.45\pm0.03$	$1.32\pm0.1$	193	$0.40\pm0.04$	$0.90\pm0.04$	128	
Blank glass	$0.76\pm0.1$	_	_	_	_	_	



Fig. 7 Percent differences in haze measurements after scratching for the uncrosslinked and crosslinked 4-quadlayer interlayer ISAM ARC's of the architecture  $[PAH_7/PAA_x/PAH_7/SiO_{29}]_{n=4.5}$ .

As the pH is lowered, the scratch resistance is increased due to strong interconnectivity of the Si NPs, however the anti-reflection properties are concomitantly reduced as a result of both the loss of void space (resulting in increased refractive index) and increased optical scattering caused by the thick and rough polyelectrolyte layers. As discussed previously, there is a sharp transition of the anti-reflection performance of the films from unsatisfactory to quite good, as the pH of PAA was increased from 5.0 to 5.2. Since the interlayer ISAM ARC with PAA<sub>5.2</sub> possesses the best scratch resistance for the films with high levels of anti-reflection, this film provides the best compromise of the optical and mechanical properties within this study. The critical load for abrasion for PAA<sub>5.2</sub> is nearly seven times larger than that for PAA<sub>6.0</sub>.

## 4. Conclusion

The alteration of the pH of PAA in PAH/PAA films and PAH/PAA/ PAH/SiO2 interlayer ionic self-assembled multilayer anti-reflection coatings was shown to strongly affect a large number of intrinsic film properties. In PAH/PAA films, we observed a distinct transition from overall exponential to linear-growth in film thickness between PAA<sub>5.4</sub> and PAA<sub>5.6</sub>. This was related to a change in the concentration of free diffusing PAA chains and resultant changes in PAH thicknesses. PAH/PAA films thermally crosslinked at a range of temperatures were examined under FTIR to confirm the establishment of covalent amide linkages between the polyelectrolyte functional groups. PAH/PAA/PAH/SiO<sub>2</sub> interlayer films were then fabricated with varying pH values of the PAA solution to examine whether the increased polyelectroyte thickness and interconnectivity combined with thermal crosslinking could improve the abrasion resistance of Si nanoparticle anti-reflection coatings. All of the interlayer ISAM ARCs were thermally crosslinked before analysis. It was found through FESEM of the PAH/PAA/PAH/SiO2 interlayer films that the increased polyelectrolyte thicknesses became especially apparent at pH values of 3.0 and 4.0. At a pH of 3.0 for PAA, the RMS surface roughness and optical scattering rose dramatically in both PAH/PAA and interlayer ISAM ARCs. Large microporous polyelectrolyte

structures formed due to low degree of ionization of PAA. Antireflection (transmittance maxima and reflectance minima) in interlayer ISAM ARCs showed a definitive correlation with the PAA pH, with a shift from excellent to unsatisfactory anti-reflection behavior from PAA<sub>5.2</sub> to PAA<sub>5.0</sub>. The scratch resistance in the interlayer ISAM ARCs continuously improved as the pH of PAA was decreased, leading to increased polyelectrolyte thickness and interconnectivity. Interlayer ISAM ARCs fabricated at PAA52 exhibited both excellent anti-reflection and order-of-magnitude improvement in scratch resistance compared to PAA<sub>6.0</sub>. This interlayer ISAM ARC at PAA<sub>5.2</sub> had a transmittance maximum and reflectance minimum of 98.81% and 0.14%, respectively. Below a pH of 5.2 for PAA, the strongly interconnected polyelectrolyte network yielded increased mechanical robustness but the accompanying optical scattering and increased refractive index due to decrease in void space rendered the films unsuitable as anti-reflection coatings. The Lc1 critical load for abrasion at a PAA pH of 5.2 was nearly seven times larger than for pH 6.0 but almost four times lower than for pH of 3.0, as determined through micro-scale scratching testing (triboindentation). In testing the haze and the macroscopic scratch testing, the interlayer ISAM ARC with PAA<sub>6.0</sub> had more than a factor of 2 greater change in haze after scratching compared to PAA5.2. All of the crosslinked films showed an increase in scratch resistance compared to uncrosslinked films, as shown by smaller changes in haze after scratching. In short, this work emphasizes that relatively small changes in the fabrication parameters can have dramatic impact on both the optical and mechanical properties of layer-by-layer anti-reflection coatings incorporating polyelectrolytes and silica nanoparticles.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by the Army Research Laboratory, under Cooperative Agreement Number W911NF-06-2-0014. The authors gracefully acknowledge several individuals who substantially aided in the experimental methods, including microscopy support by Steve McCartney at the Virginia Tech ICTAS NCFL, ellipsometry guidance from Neha Singh and Nina Hong at J. A. Woollam Co., and TriboIndenter support from Jacob Noble at Hysitron Co. The authors acknowledge the assistance of Tom Wertalik and Eric Seeh in the processing of substrates required for this work. The authors also acknowledge Professor Herve Marand and Hadi Mohammadi for access and assistance with the BYK Gardner Haze Meter, and Professor Hans Robinson for use of his motorized translational stage.

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