# Quantized Nanolaminates through the microscope -

# A step forward in optical thin film technology?

Evatec's Principal Scientist *Dr. Silvia Schwyn Thoeny* introduces quantized nanolaminates, tells us the potential benefits for optical thin film production and how they can be manufactured effectively by sputter technology on CLUSTERLINE<sup>®</sup> 200 BPM.



### Why Quantized Nanolaminates?

Optical interference coatings such as anti-reflection, mirror or filter coatings are based on stacks of materials with at least 2 different refractive indices, n. The interference effect is stronger if the difference in refractive index between materials is larger. Hence, a stack design based on materials with a larger difference in refractive index requires a smaller number of individual layers and thus less overall thickness to fulfill the same specification as a design based on materials with a smaller difference. In addition to the refractive index, the materials have to fulfill other requirements, among those being transparency with negligible losses in the wavelength range of interest.

However, in dielectric materials the refractive index and absorption edge are linked. Materials with high refractive index have their absorption edge at a long wavelength, while low refractive index materials have the absorption edge at a short wavelength. TiO<sub>2</sub> is the dielectric material with the highest refractive index, which is transparent in the visible range of the spectrum starting to transmit at ca. 400 nm. Having a material at disposition with a higher refractive index while being transparent in the VIS would be of broad practical relevance, since it would allow interference designs with a lower number of layers and reduced overall thickness.

An approach to overcome the connection between the two characteristics is Quantized Nano Laminates (QNL). In this concept thin layers of high and low refractive index with a thickness in the nanometer range or below are stacked. The limited structure size leads to a change of the energy gap, which can be adjusted by the physical thickness of the materials, whereas the thickness ratio of the materials determines the effective refractive index of the QNL.

In optical interference coatings, the decoupling of band gap and refractive index potentially offers the advantage of using the QNL material combination instead of using a specific material. The stack structure of a typical coating with QNL in comparison with standard interference is illustrated in Figure 1.



Figure 1: Comparison of film structure

As an example, in the UV range the band gap of Ta<sub>2</sub>O<sub>5</sub> can be pushed towards shorter wavelength and can thus replace the use of HfO<sub>2</sub>. This is desirable since hafnium targets are expensive and because HfO<sub>2</sub> has a tendency to form polycrystalline films with grain boundaries which can cause losses by straylight. Another very interesting material combination is QNL composed of amorphous silicon and SiO<sub>2</sub> which offers a higher effective index than TiO<sub>2</sub> with being transparent well into the visible part of the spectrum.

### Nanolaminates Benefits

Table 1 summarizes the potential benefits of nanolaminates when it comes to optical thin film production. Key to commercial realization is finding a practical production technique and that's where sputtering comes in. Although ALD and IBS lead to good results, they do have drawbacks with regard to volume production, whereas magnetron sputtering achieves deposition rates comparable to standard optical thin film production processes.

# Potential benefits of quantized nanolaminates Decoupling of refractive index and absorption edge Extending useful range of high index materials Improved film performance Comparable results achieved with less complex stacks / shorter process times Replacement of expensive materials In-situ PEM and optical monitoring can be used just like in classical processes

## *Now you really can 'have your cake and eat it'*

### Production solutions on CLUSTERLINE® 200 BPM

Evatec's CLUSTERLINE<sup>®</sup> 200 BPM dynamic sputter tool with its large substrate table is well suited to nanolaminates deposition. The deposition system has a capacity of 15 substrates of diameter 200mm. Substrate loading and unloading is executed automatically through a vacuum transfer module and load-lock. The system is also equipped with broad band and monochromatic optical monitoring.

For the deposition of aSi - SiO<sub>2</sub> QNL one sputter source was equipped with a silicon target with the purpose to deposit an amorphous silicon layer. The SiO<sub>2</sub> layer is formed by the plasma source (PSC), where the aSi film partially gets oxidized by the oxygen plasma. The plasma source is a RF-driven capacitively coupled discharge, where oxygen as operating gas is partially dissociated and ionized. The schematic tool configuration is shown in Figure 2.

When depositing the long pass filter consisting of  $aSi - SiO_2 QNL$  as the high refractive index material and  $SiO_2$  for the low refractive index material, a second sputter station equipped with a silicon target was used to reactively deposit the low index  $SiO_2$  layers.

The turntable configuration is perfectly suited for the deposition of QNLs. The substrates pass repeatedly beneath the active sources, thereby exposing the substrates to both the sputter (Si & Ta) and the plasma source with each rotation. The total thickness deposited in one turn is determined by the rotation speed of the table, a parameter which can easily be varied in a wide range, and the deposition rate. The thickness ratio of the aSi and SiO<sub>2</sub> materials is determined by the sputter and the plasma source power, which can be adjusted individually. Deposition rates for QNL layers tend to be as high as those for single aSi since the active source is run at standard conditions. Load substrates e.g. 15x 8" PSC Unload e.g. 1 Material 1: Material 2: PSC Ta₂O₅ SiO<sub>2</sub> **Continuous rotation Continuous rotation** Optional of turntable of turntable Stabilizes process Deposition of Deposition of 0.1-3nm per pass 0.1-3nm per pass Set by table speed Set by table speed **Ratio of materials Ratio of materials** by source power by source power Figure 2: CLUSTERLINE® 200 BPM

### **Experimental results**

### 1. Illustrating the quantized nanolaminate effect

In a first experiment, the Si and Ta sources were run at fixed powers. The table speed was varied from 3 to 15 seconds per pass, which means that the thickness ratio of high to low layers stayed constant, but the individual layer thickness increased with the slower table speed. The well thickness, i.e. thickness of Ta<sub>2</sub>O<sub>5</sub> was determined to be in the range of 0.2-1 nm. According to the theory it was expected that the absorption edge would shift towards shorter wavelengths the thinner the individual well layers became, whereas the effective refractive index would remain constant for all five samples. This behavior was indeed seen in the transmission measurements. The absorption edge of the 3s/pass sample lies at the shortest wavelength, whereas the 15s/pass results in the longest wavelength edge with a difference of 18 nm between the samples (see Figure 3). For reference the absorption edge of a Ta<sub>2</sub>O<sub>2</sub> layer is indicated by a dotted line. In the longer wavelength range above 280 nm, all curves overlay since they all have the same effective refractive index and optical thickness. Furthermore, they touch the solid line for 1/2  $\lambda$  optical thickness indicating very low absorption of the QNLs in the longer wavelength range.



Figure 3: Transmittance of QNL layers with the same thickness ratio of Ta<sub>2</sub>O<sub>5</sub> to SiO<sub>2</sub>, but with increasing table speeds. The thinnest layers deposited with the highest table speed show the largest shift in absorption edge to shorter wavelength.

### 2. AR Coating

In a second experiment, a UV AR coating centered on 266nm was deposited on silica substrates using a stack comprising SiO, and QNL of TaO<sub>2</sub>/SiO<sub>2</sub> showing an effective coating without the use of Hafnia. The reflectance and transmission performance on a double side coated sample are shown in Figure 4.



Figure 4: Transmittance and reflectance measurements of the antireflective coating of SiO2 and QNL layers showing excellent transmission at 266 nm

### 3. Mirror at 355nm with short pass filter

Figure 5 shows a comparison of performance for two short pass filters: the curve in red is a standard SiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> coating. Both designs reflect at 355nm and transmit light at shorter wavelength, but transmittance falls off rapidly below 300nm using standard filter designs whereas quantized nanolaminate structure enables significantly higher light output down close to 280nm.



Figure 5: Short pass filter transmittance of a design using SiO<sub>2</sub>-QNL (green) compared to standard coating (red) using SiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>

### 4. Long pass filter

In Figure 6 we see a comparison between long pas filters both having 16 layers. The classical design using TiO<sub>2</sub> / SiO<sub>2</sub> blocks only from 520 to 670nm and would require twice the number of layers to give equivalent performance to the QNL design using aSi/SiO<sub>2</sub>. This shows how QNL structures can reduce overall coating thickness, deposition times and manufacturing costs.



Figure 6: Transmittance of a long pass filter based on SiO<sub>2</sub>/QNL aSi-SiO<sub>2</sub> and on SiO<sub>2</sub>-TiO<sub>2</sub> for comparison

### **Quantized nanolaminate: the theory**

In standard dielectric materials the refractive index and the energy of the absorption gap are fundamentally linked. Quantized nanolaminates however allow us to set the refractive index and the absorption edge independently within the limits given by the bulk properties of the high and low index material.



Figure 7: Periodic structure of high and low band gap areas, which limit the electron mobility

The theory of the quantized nanolaminates has already been detailed in other publications but here is a quick summary. As already mentioned, optical coatings mostly produce amorphous or polycrystalline materials whose band structure is not clearly defined, nevertheless an energy gap between quasi-free ground states and higher conduction states is present. Thus, the band gap itself can be regarded as a depletion zone of states and the densities between bound and free states are so low that they can be neglected. Thus, the potential well, which is necessary for the quantization is clearly defined.

The electron mobility can be limited in the growth direction if two materials with high and low band gap are combined in a thin periodic structure. In this case the low index material will act as a barrier, whereas the high index material acts as the guantum well, as illustrated in Figure 7. Since this is a simple potential consideration, even non-closed atomic layers can lead to a suitable periodic potential.

The thickness of the quantum well will determine the shift in band gap, whereas the thickness ratio of high to low bandgap material will determine the refractive index. Thus, the novel concept of so-called quantizing nanolaminates (QNLs) allows for independent adjustment of the optical band gap and the refractive index. To give an idea of the thicknesses required we turn to data published for SiO<sub>2</sub>- $Ta_2O_5$  which shows that the quantum well layers should be much smaller than 2 nm to achieve a shift which is of practical use.

Please take a look at the open access paper published in Optics Express and Advanced Photonic Research to access more references of previous work reported in the literature about Quantized Nanolaminates and more results for the work being done at Evatec.



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