Buffer Layer Optimization

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Introduction

We are studying the effect of using different kinds of PEDOT in the PEDOT:PSS buffer layer on the device's photon absorption and internal optical electrical field distribution. We will also determine the ITO thickness that optimizes these parameters.

We will be using Transfer Matrix Formalism (TMF) to evaluate these properties, which is explained [here (https://aip.scitation.org/doi/abs/10.1063/1.370757)](https://aip.scitation.org/doi/abs/10.1063/1.370757), and summarized below.

Theory behind TMF

Interface Matrices

Each interface in the structure (between layers j and k) can be described by an interface matrix of the form:

$$I_{jk} = \frac{1}{t_{jk}}\begin{bmatrix} 1 & r_{jk} \\ r_{jk} & 1 \end{bmatrix}$$

where r_{jk} and t_{jk} are the Fresnel complex *reflection* and *transmission* coefficients at interface jk.

These coefficients are given by:

$$r_{jk} = \frac{q_j - q_k}{q_j + q_k},$$

$$t_{jk} = \frac{2q_j}{q_j + q_k}$$

where

$$q_j = [\tilde{n}_j^2 - \eta_0^2 sin\phi_0]^{\frac{1}{2}}$$

We assume that ϕ_0 is 0, so q_j is simplified to $\tilde{n}_j$ - the complex index of refraction of layer j, which is determined experimentally:

$$q_j = \tilde{n}_j = \eta_j + ik_j.$$

where η_j and k_j are the refractive index and extinction coefficient of layer j.

Layer Matrices

The layer matrix describing the propagation through layer j is given by:

$$L_j = \begin{bmatrix} e^{-i\xi_j d_j} & 0 \\ 0 & e^{i\xi_j d_j} \end{bmatrix}$$

where

$$\xi_j = \frac{2\pi}{\lambda} q_j$$

and $\xi_j d_j$ is the *layer phase thickness*, corresponding to the phase change the wave experiences as it traverses layer j.

System Transfer Matrix

By using the interface and layer matrices, the total system transfer matrix (scattering matrix) S can be written:

$$S = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} = (\prod_{v=1}^{m} I_{(v-1)v} L_v) I_{m(m+1)}$$

This matrix relates the electric field at the ambient side and susbstrate side (Aluminum cathode - layer m+1) by:

$$\begin{bmatrix} E_0^+ \\ E_0^- \end{bmatrix} = S \begin{bmatrix} E_{m+1}^+ \\ E_{m+1}^- \end{bmatrix}$$

where the optical electric field at any point in the system is resolved into two components: one component propagating in the positive x direction and one in the negative x direction, which at a position x in layer j are denoted $E_j^+(x)$ and $E_j^-(x)$

For the total layered structure, the resulting complex reflection and transmission coefficients can be expressed by using the matrix elements of the total system transfer matrix:

$$r = \frac{E_0^-}{E_0^+} = \frac{S_{21}}{S_{11}},$$

$$t = \frac{E_{m+1}^+}{E_0^+} = \frac{1}{S_{11}}.$$

Calculating Internal Electric Field

In order to calculate the internal electric field in layer j, the layers can be divided into two subsets: one subset to the left of j which will be represented by S'_j, and one subset to the right of j which we'll represent with S''_j.

The total system transfer matrix can then be written as

$$S = S'_j L_j S''_j$$

The partial system transfer matrix for the layers left of j is equal to

$$S'_j = \begin{bmatrix} S'_{j11} & S'_{j12} \\ S'_{j21} & S'_{j22} \end{bmatrix} = (\prod_{v=1}^{j-1} I_{(v-1)v} L_v) I_{(j-1)j}.$$

For the layers right of j, the matrix is

$$S''_j = \begin{bmatrix} S''_{j11} & S''_{j12} \\ S''_{j21} & S''_{j22} \end{bmatrix} = (\prod_{v=j+1}^{m} I_{(v-1)v} L_v) I_{m(m+1)}.$$

The expression for the total electric field at distance x from the left boundary of layer j is:

$$E_j(x) = \frac{S''_{j11} \cdot e^{-i\xi_j(d_j - x)} + S''_{j21} \cdot e^{i\xi_j(d_j - x)}}{S'_{j11} S''_{j11} \cdot e^{-i\xi_j d_j} + S'_{j12} S''_{j21} \cdot e^{i\xi_j d_j}} E_0^+,$$

where $0 \leq x \leq d$.

Calculation

Setting up constants

In [1]:
```
import numpy as np
from matplotlib import pyplot as plt
import math
import cmath
import copy

wavelength = 632.8 # nm
m = 3 # no. of layers between ambient and substrate
```

Interface Matrices

In [2]:

```
# Determined optical properties of [Ambient, ITO, Buffer, Active, Cathode (sub
strate)]
eta = np.array([1.0003, 1.8355, 1.44846, 1.77, 1.37166]) # refractive indices
k = np.array([0, 0.012236, 0.05354, 0.1192994, 7.60477]) # extinction coeffici
ents
n = eta + 1j*k # complex indices of refraction
q = n # since we are assuming that the angle of incidence is 0

# Fresnel complex coefficients
# t[0] corresponds to t_01 in the above theory
t = [] # transmission
r = [] # reflection

for j in range(len(q) - 1):
    k = j+1
    t_jk = (2 * q[j]) / (q[j] + q[k])
    r_jk = (q[j] - q[k]) / (q[j] + q[k])
    t.append(t_jk)
    r.append(r_jk)

t = np.array(t)
r = np.array(r)

# The interface matrices will be calculated inline using these values rather t
han creating them all now in a 3-D array.
```

Layer Matrices

In [3]:

```
# Layer phase thicknesses of [Ambient (for consistent indices), ITO, Buffer, A
ctive, Cathode]
d = [float("inf"), 130, 50, 110, 50]
xi = q * (2 * math.pi / wavelength)
xi[0] = float("inf")

# The layer matrices will be calculated inline using these values rather than
 creating them all now in a 3-D array.
# Note that we set the values corresponding to the ambient to infinity, since
 these are just placeholders to achieve consistent
# indexing, and should not be used.
```

Scattering Matrices

In [4]:
```
# Returns the scattering matrix corresponding to the given layers
def scattering_matrix(start_layer, stop_layer, trans, refl, thick, phase):
    prod = np.identity(2) # initial value of cumulative product
    for v in range(start_layer, stop_layer+1):
        # interface matrix I_(v-1)v
        t_jk = trans[v-1]
        r_jk = refl[v-1]
        I_v = (1 / t_jk) * np.array([
                                [1, r_jk],
                                [r_jk, 1]
                            ])

        # layer matrix L_v
        phase_thickness = phase[v] * thick[v]
        L_v = np.array([
                        [cmath.exp(-1j*phase_thickness), 0],
                        [0, cmath.exp(1j*phase_thickness)]
                    ])

        inner_prod = np.matmul(I_v, L_v)

        prod = np.matmul(prod, inner_prod) # update cumulative product

    outer_interface = (1 / trans[stop_layer]) * np.array([
                                                            [1, refl[stop_laye
r]],
                                                            [refl[stop_layer],
1]
                                                        ])
    return np.matmul(prod, outer_interface)
```

Optimizing the internal optical electric field

Here, we calculate the distribution of the normalized modulus squared of the incident optical electric field of the device using two different buffer layers.

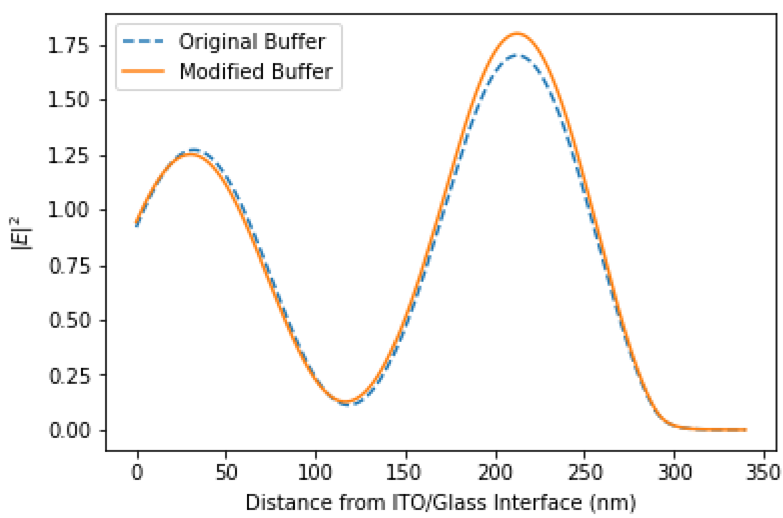
In [5]:
```
# Returns the electric field at point x in layer j, given the partial scatteri
ng matrices.
def electric_field(S_left, S_right, j, x, thick, phase):
    exp_1 = cmath.exp(-1j*phase[j] * (thick[j]-x))
    exp_2 = cmath.exp(1j*phase[j] * (thick[j]-x))
    numerator = (S_right[0][0] * exp_1) + (S_right[1][0] * exp_2)

    exp_3 = cmath.exp(-1j*phase[j]*thick[j])
    exp_4 = cmath.exp(1j*phase[j]*thick[j])
    denominator = (S_left[0][0] * S_right[0][0] * exp_3) + (S_left[0][1] * S_r
ight[1][0] * exp_4)

    return numerator/denominator
```

Modified buffer layer parameters

In [6]:
```
# Determined optical properties of [Ambient, ITO, Modified Buffer, Active, Cat
hode (substrate)]
eta_mod = np.array([1.0003, 1.8355, 1.34846, 1.77, 1.37166]) # refractive indi
ces
k_mod = np.array([0, 0.012236, 0.05354, 0.1192994, 7.60477]) # extinction coef
ficients
n_mod = eta_mod + 1j*k_mod # complex indices of refraction
q_mod = n_mod # since we are assuming that the angle of incidence is 0

# Fresnel complex coefficients
# t[0] corresponds to t_01 in the above theory
t_mod = [] # transmission
r_mod = [] # reflection

for j in range(len(q_mod) - 1):
    k = j+1
    t_jk = (2 * q_mod[j]) / (q_mod[j] + q_mod[k])
    r_jk = (q_mod[j] - q_mod[k]) / (q_mod[j] + q_mod[k])
    t_mod.append(t_jk)
    r_mod.append(r_jk)

t_mod = np.array(t_mod)
r_mod = np.array(r_mod)
xi_mod = q_mod * (2 * math.pi / wavelength)
xi_mod[0] = float("inf")
```

Electric field comparison

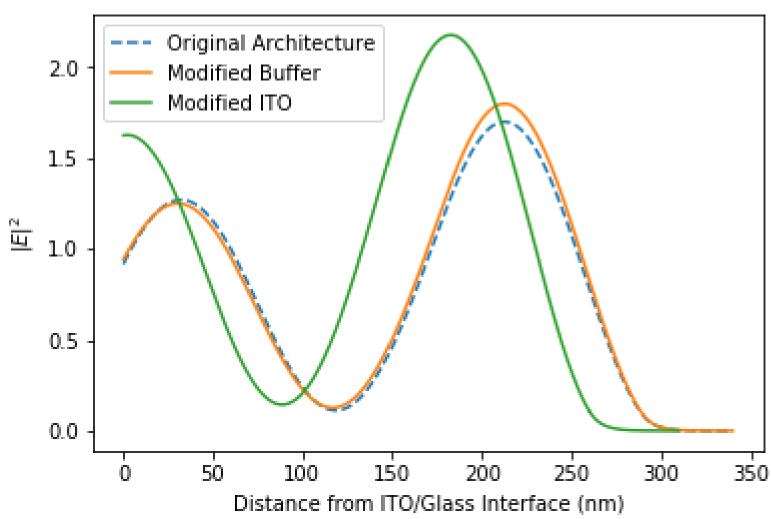
In [7]:
```
E = []
E_mod = []
position = []
current_position = 0
for j in range(1, m+2):
    # To the left of j:
    S_left = scattering_matrix(1, j-1, trans=t, refl=r, thick=d, phase=xi)
    S_left_mod = scattering_matrix(1, j-1, trans=t_mod, refl=r_mod, thick=d, p
hase=xi_mod)

    # To the right of j:
    S_right = scattering_matrix(j+1, m, trans=t, refl=r, thick=d, phase=xi)
    S_right_mod = scattering_matrix(j+1, m, trans=t_mod, refl=r_mod, thick=d,
phase=xi_mod)

    # Electric field in j:
    x_j = np.linspace(0, d[j], 200) # values for position in this layer
    position.extend(x_j + current_position)
    current_position += d[j]
    for x in x_j:
        E.append(electric_field(S_left, S_right, j, x, thick=d, phase=xi))
        E_mod.append(electric_field(S_left_mod, S_right_mod, j, x, thick=d, ph
ase=xi_mod))

E_norm = np.array(np.abs(E)**2)
E_mod_norm = np.array(np.abs(E_mod)**2)
plt.plot(position, E_norm, label="Original Buffer", linestyle='--')
plt.plot(position, E_mod_norm, label="Modified Buffer")
plt.xlabel("Distance from ITO/Glass Interface (nm)")
plt.ylabel(r'$|E|^2$')
plt.legend()
plt.show()
```



Further optimizing the internal optical electric field

Here, we once again calculate the normalized modulus squared of the incident optical electric field of the device, this time using ITO of various thicknesses.

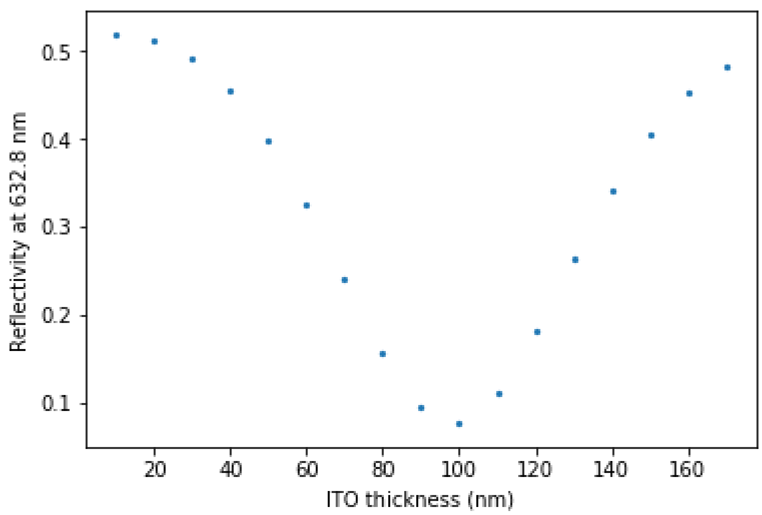
In [8]:
```
d_mod = [-1, 100, 50, 110, 50]
E_ito_mod = []
position_ito_mod = []
current_position = 0
for j in range(1, m+2):
    # To the left of j:
    S_left = scattering_matrix(1, j-1, trans=t, refl=r, thick=d_mod, phase=xi)

    # To the right of j:
    S_right = scattering_matrix(j+1, m, trans=t, refl=r, thick=d_mod, phase=xi
)

    # Electric field in j:
    x_j = np.linspace(0, d_mod[j], 200) # values for position in this layer
    position_ito_mod.extend(x_j + current_position)
    current_position += d_mod[j]
    for x in x_j:
        E_ito_mod.append(electric_field(S_left, S_right, j, x, thick=d_mod, ph
ase=xi))

E_ito_mod_norm = np.array(np.abs(E_ito_mod)**2)
plt.plot(position, E_norm, label="Original Architecture", linestyle='--')
plt.plot(position, E_mod_norm, label="Modified Buffer")
plt.plot(position_ito_mod, E_ito_mod_norm, label="Modified ITO")
plt.xlabel("Distance from ITO/Glass Interface (nm)")
plt.ylabel(r'$|E|^2$')
plt.legend()
plt.show()
```



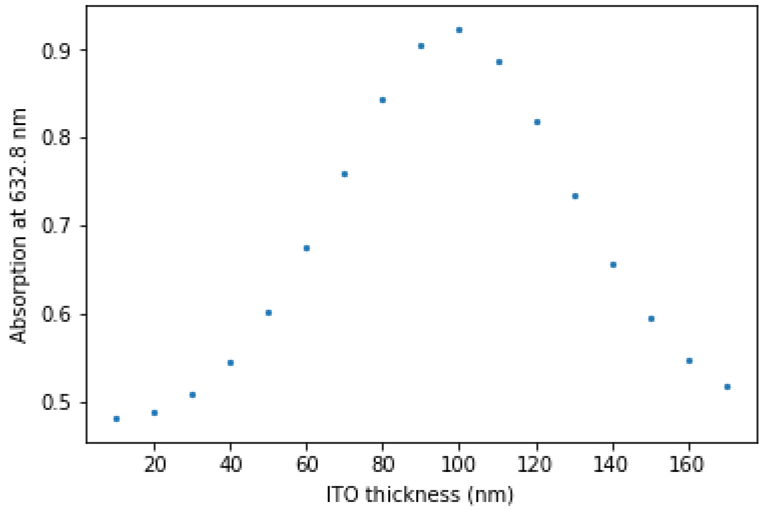
Optimizing photon absorption

Here, we calculate the absorption and reflectance of the device using various ITO thicknesses.

In [9]:
```
ito_thicknesses = np.arange(10, 180, 10) # thicknesses of ITO layer to be test
ed
layer_thicknesses = copy.copy(d) # shallow copy so we don't change d
R = []
A = []
for d_ito in ito_thicknesses:
    layer_thicknesses[1] = d_ito
    S = scattering_matrix(start_layer=1, stop_layer=m, trans=t, refl=r, thick=
layer_thicknesses, phase=xi)
    r_complex = S[1][0] / S[0][0]
    reflectivity = np.abs(r_complex)**2
    R.append(reflectivity)
    A.append(1 - reflectivity)
plt.scatter(ito_thicknesses, R, s=5)
plt.xlabel("ITO thickness (nm)")
plt.ylabel("Reflectivity at 632.8 nm")
plt.show()
```



In [10]:
```
plt.scatter(ito_thicknesses, A, s=5)
plt.xlabel("ITO thickness (nm)")
plt.ylabel("Absorption at 632.8 nm")
plt.show()
```



In [ ]: