ISSN : 0974 - 7486 Volume 9 Issue 5

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 9(5), 2013 [187-191]

Color space chromaticity diagram: Estimation of Co impurity ratios in SnO_2 thin films

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ABSTRACT

This paper present the computation and analysis of CIE spectral tristimulus values X,Y and Z to estimate impurity ratios in thin film. White light illumination D65 and 2 º field of view were selected to study color sensation and color matching of SnO_2 thin film doped with various impurity ratios (1,3,5 and 7%) of Co. Results are displaced as a 1931 CIE chromatic diagram.

KEYWORDS

Color science;
CIE;
Goldlike coatings;
Data storage.

INTRODUCTION

Metal oxide has become widely used in many applications[1]. Color is an aspect of visual perception that is not easy to define or to measure. It is a sensation whereby a human observer can see differences between two fields of view, that are distinguished by spectral composition differences in the observed radiant energies[2-4]. Hence color is:

- A sensation, dependent upon the observer of interest only if the observer can distinguish differences caused by spectral (wavelength-dependent) energy compositions (distributions).
- The spectral energy compositions that are sensed by the eye/brain system of the human observer, result from both: Sources of light, and objects that modify light.

Experienced technicians and researchers are accustomed to estimating a film's thickness simply by observing its color. Thus slight changes in the thickness of these films create major shifts in their perceived color[5]. This color change is caused by variations in the reflectance of the thin dielectric film with wavelength[6]. Whilst many reports have considered the colors in thin films. Niyomsoan et al. (2002)[7] study the color variation in ZiN and TiN with respect to the atomic ratio between nitrogen and transition metals and oxygen as the contaminant. The prepared films were controlled at 0.5 mm using cathode arc evaporation methods. Their color was quantized in the L*a*b* color system as a replacement for gold –like coatings and in decorative coatings. Henrie *et.al.*(2004)[8], presents the calculation of the perceived color of dielectric films on silicon. Their computation perceives color for an arbitrary light source, light incident angle, and film thickness. Then the calculated color is converted in to RGB parameters displayed on a color monitor, resulting in the generation of electronic color chart for dielectric films.

Lin *et.al.* (2011)[9] study the color effects of optical antireflection film irradiated by 60 KeV protons to be used in space optical system. Macleod[10] discuss optimal; color stimuli applied to multilayer coatings during the plot of chromaticity coordinate and the variation of color as the coating is tilted from normal. Tielly (2011)[11] discuss the, the active data storage layer (or layers) on CDs, DVDs, HD-DVDs and Blue-Ray discs is reflective. Data is stored by making small dots on the recording layer that have a different reflectivity to the background. The writing process involves decreasing the reflectivity and the reading process involves detecting these reflectivity differences. In this article, we calculate the perceived color variation due to adding impurity to thin film and displaced as *xy*-chromatic diagram.

THREE-STIMULUS GENERATION

Mathematically the above physical and physiological description of color can be expressed in the following manner. Any light source S with spectral radiometric flux $P(\lambda)$ generates three main stimuli in a human eye: red (r), green (g), and blue (b). The relative "strength" o f each can be estimated by the integrals.

$$r = \int P(\lambda)R(\lambda)d\lambda \; ; g = \int P(\lambda)G(\lambda)d\lambda \; ; b = \int P(\lambda)B(\lambda)d\lambda \qquad (1)$$

Where $R(\lambda)$, $G(\lambda)$, and $B(\lambda)$ are the spectral sensitivity of the three pigments of the eye shown in Figure 1 (term them as natural primaries).

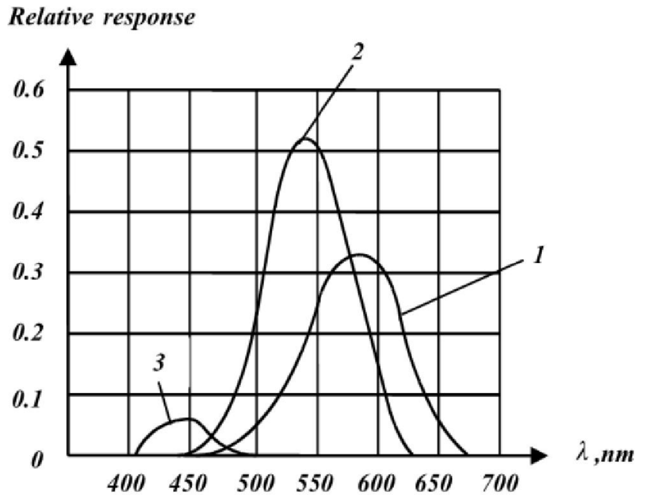
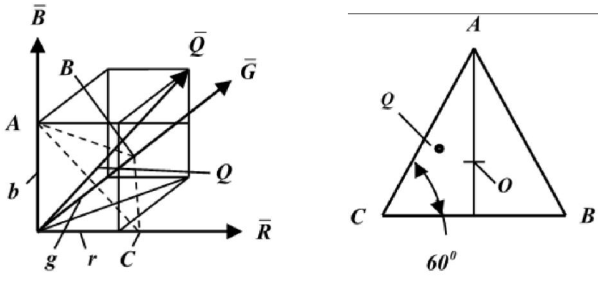


Figure 1 : Relative spectral sensitivity of three kinds of photoreceptors: 1, *R(λ)*, cones with erythrolabe; 2, *G(λ)*, cones with chlorolabe; 3, *B(λ)*, cones with cyanolabe.

Perception of all three stimuli creates the feeling of color, Q, of the light source S. This color can be represented by its vector.

$$\bar{Q} = r\,\bar{R} + g\,\bar{G} \; + b\,\bar{B} \qquad (2)$$

And by a corresponding point Q(r, g, b) in the 3-D color space shown in Figure 2a. Hence, r, g, and b are considered as color coordinates of the color Q and therefore of the light source S.



a) b)

Figure 2 : (a) 3-D color space and (b) its 2-D presentation in a single plane.

Another set of primaries was suggested and adopted by the International Commission on Illumination (CIE)[12]. These primaries are based on the standardized color mixture curves, sometimes termed color matching functions[4,6]. The curves are shown in Figure 3.

In terms of colormixture curves the tristimulus values related to the light source S are as follows:

$$X\text{=const} \int_{0.38}^{0.77} P(\lambda)\bar{x}(\lambda)\,d\lambda; \quad Y\text{=const} \int_{0.38}^{0.77} P(\lambda)\bar{x}(\lambda)\,d\lambda; \quad Z\text{=const} \int_{0.38}^{0.77} P(\lambda)\bar{x}(\lambda)\,d\lambda; \qquad (4)$$

And they are usually converted to the normalized color coordinates x, y, and z :

$$x = \frac{X}{X+Y+Z}; \quad y = \frac{Y}{X+Y+Z}; \quad z = \frac{Z}{X+Y+Z} \qquad (5)$$

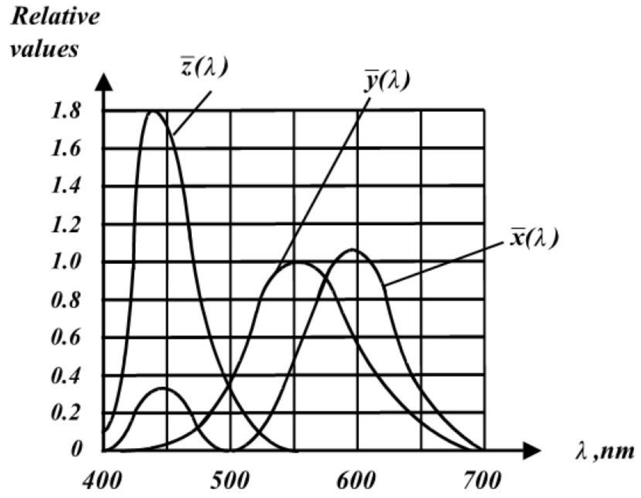


Figure 3 : Color mixture curves (standardized by the CIE)[11].

Evidently $x + y + z = 1$, so that only two coordinates, say x and y, are enough to characterize the color of an object. The corresponding x, y-diagram is shown in Figure 4. The “gray” color, or no color at all, is defined as a situation when all three normalized color coordinates are equal: X = Y = Z. In terms of *x*, *y*, and *z* this means:

$$x_g=y_g=z_g=0.33 \qquad (6)$$

This case is related to point O in Figure 4. All gray levels, from black to white, are represented in this point.

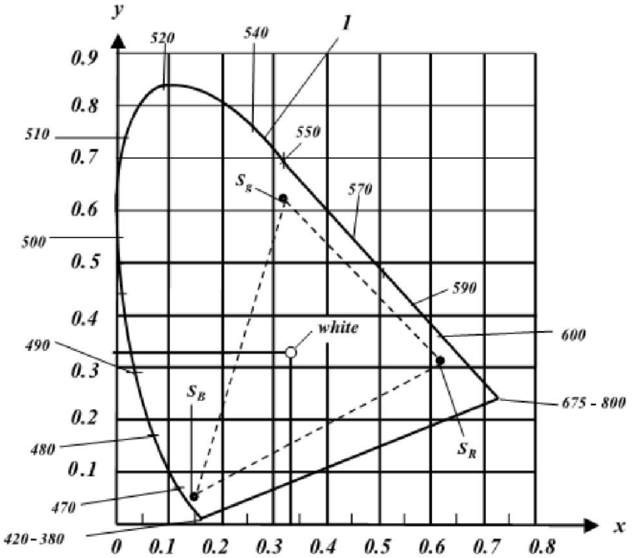


Figure 4 : x, y-diagram of colors (the CIE chromaticity diagram).

EXPERIMENTAL DETAILS

SnO_2:Co thin films were obtained by the spray pyrolysis in air atmosphere. A homogeneous solution was prepared by dissolving ($SnCl_4.5H_2O$)and ($CoCl_2$) in redistilled water at room temperature in which the volumetric ratios of Co were (1,3,5 and 7)% The glass substrate were cleaned with ethanol and acetone in an ultrasonic cleaner. The optimized deposition parameters such as spray nozzle-substrate distance (30 cm), spray time (10 s) and the spray interval (80 s) were kept constant during the deposition process. The resultant solution was sprayed onto the preheated substrate at 500 °C. The total duration of film coating was adjusted to get film thickness of a bout 400 nm.

RESULTS AND DISCUSSION

Color computation

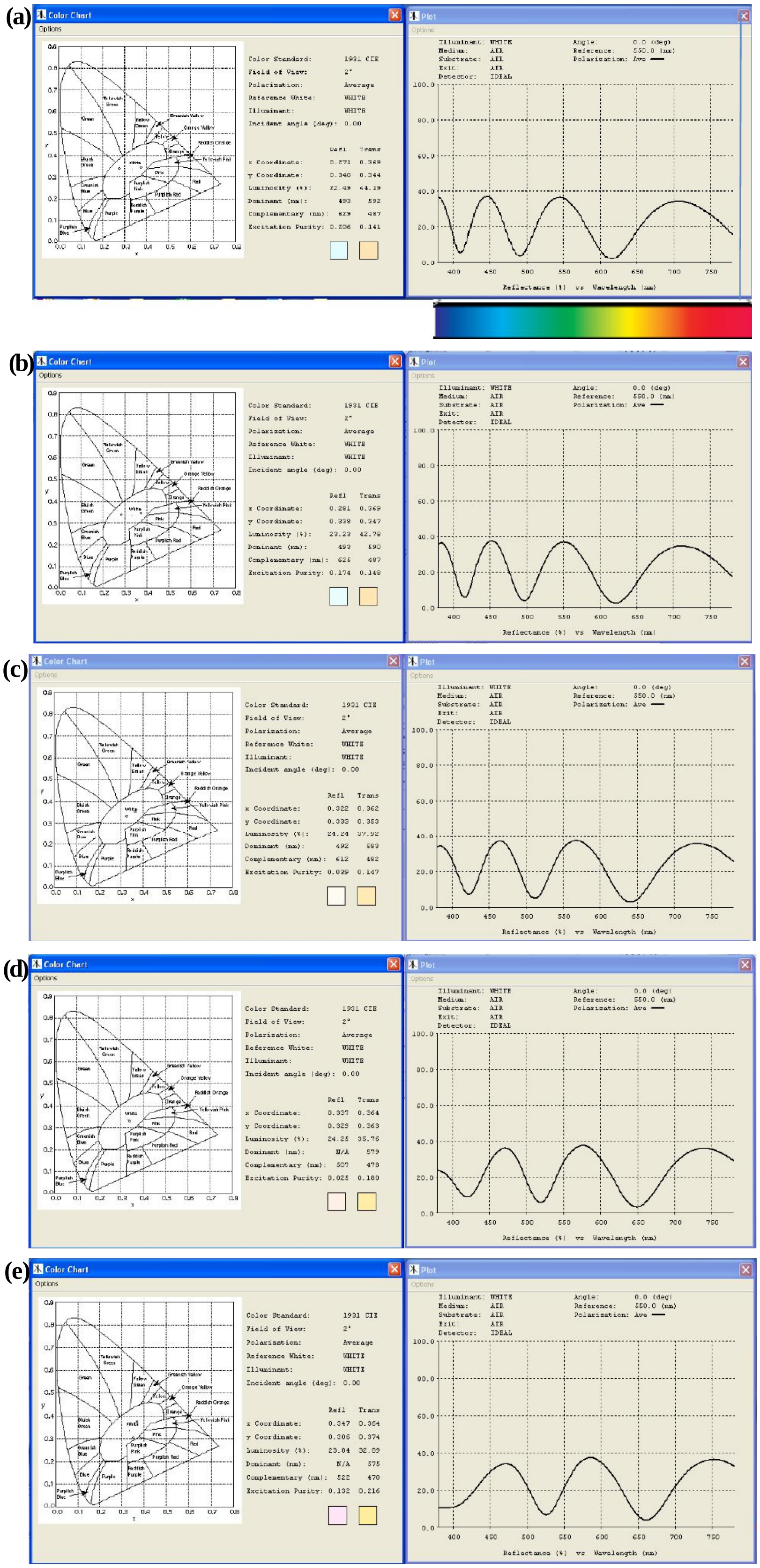
The basic process used to calculate RGB parameters for an arbitrary film thickness and viewing angle can be broken up into *two steps*[8]: *First*, the reflected power as a function of wavelength is calculated, this can be done using a standard thin film matrix approach[6]. *Second*, with the aid of equations(1-5) the response of the eye is taken into account to calculate the CIE *XYZ* parameters from wavelength spectrum.

We try to extend the previous work[8], and study film color variation due to impurity ratios by evaluating CIE *XYZ* parameters. As an example SnO2 thin film of ~ 400nm thickness and Co as impurity with 1,3,5and 7% ratios were selected and deposited using spray pyrolisis method. The coating were analyse from 380nm to 780nm in 5 nm increments. The tristimulus values are calculated by the spectral integration of the following wavelength dependent data functions:

- A selected CIE illuminate was D65 (represents daylight but not direct sunlight).
- An object spectrophotometric measurement.
- A selected 1931 CIE standard observer (2°).

TABLE 1 : Color coordinates variation result.

COLOR PARAMETERS	*IMPURITY CONCENTRATION RATIOS (%)*									
	Reflection					*Transmission*				
	Pure	**1**	**3**	**5**	**7**	**Pure**	**1**	**3**	**5**	**7**
Chromaticity Coordinates, *x*	0.271	0.231	0.322	0.337	0.347	0.369	0.369	0.362	0.364	0.364
Chromaticity Coordinates, *y*	0.340	0.336	0.333	0.329	0.306	0.344	0.347	0.353	0.363	0.374
Luminosity (%)	22.49	23.23	24.24	24.25	23.84	44.19	42.78	37.92	35.76	32.89
Dominant wavelength (nm)	493	493	492	N/A	N/A	592	590	583	579	575
Complementary wavelength (nm)	629	625	612	507	522	487	487	482	478	470
Excitation Purity	0.206	0.174	0.039	0.025	0.132	0.141	0.148	0.147	0.180	0.216



(a)

```
Color Standard:          1931 CIE
Field of View:           2°
Polarization:            Average
Reference White:         WHITE
Illuminant:              WHITE
Incident angle (deg):    0.00

                         Refl    Trans
x Coordinate:            0.271   0.369
y Coordinate:            0.340   0.344
Luminosity (%):          22.49   44.19
Dominant (nm):             493     592
Complementary (nm):        629     487
Excitation Purity:       0.206   0.141
```

```
Illuminant:  WHITE          Angle:         0.0 (deg)
Medium:      AIR            Reference:     550.0 (nm)
Substrate:   AIR            Polarization:  Ave ——
Exit:        AIR
Detector:    IDEAL
```

(b)

```
Color Standard:          1931 CIE
Field of View:           2°
Polarization:            Average
Reference White:         WHITE
Illuminant:              WHITE
Incident angle (deg):    0.00

                         Refl    Trans
x Coordinate:            0.281   0.369
y Coordinate:            0.338   0.347
Luminosity (%):          23.23   42.78
Dominant (nm):             493     590
Complementary (nm):        625     487
Excitation Purity:       0.174   0.148
```

```
Illuminant:  WHITE          Angle:         0.0 (deg)
Medium:      AIR            Reference:     550.0 (nm)
Substrate:   AIR            Polarization:  Ave ——
Exit:        AIR
Detector:    IDEAL
```

(c)

```
Color Standard:          1931 CIE
Field of View:           2°
Polarization:            Average
Reference White:         WHITE
Illuminant:              WHITE
Incident angle (deg):    0.00

                         Refl    Trans
x Coordinate:            0.322   0.362
y Coordinate:            0.333   0.353
Luminosity (%):          24.24   37.92
Dominant (nm):             492     583
Complementary (nm):        612     482
Excitation Purity:       0.039   0.147
```

```
Illuminant:  WHITE          Angle:         0.0 (deg)
Medium:      AIR            Reference:     550.0 (nm)
Substrate:   AIR            Polarization:  Ave ——
Exit:        AIR
Detector:    IDEAL
```

(d)

```
Color Standard:          1931 CIE
Field of View:           2°
Polarization:            Average
Reference White:         WHITE
Illuminant:              WHITE
Incident angle (deg):    0.00

                         Refl    Trans
x Coordinate:            0.337   0.364
y Coordinate:            0.329   0.363
Luminosity (%):          24.25   35.76
Dominant (nm):             N/A     579
Complementary (nm):        507     478
Excitation Purity:       0.025   0.180
```

```
Illuminant:  WHITE          Angle:         0.0 (deg)
Medium:      AIR            Reference:     550.0 (nm)
Substrate:   AIR            Polarization:  Ave ——
Exit:        AIR
Detector:    IDEAL
```

(e)

```
Color Standard:          1931 CIE
Field of View:           2°
Polarization:            Average
Reference White:         WHITE
Illuminant:              WHITE
Incident angle (deg):    0.00

                         Refl    Trans
x Coordinate:            0.347   0.364
y Coordinate:            0.306   0.374
Luminosity (%):          23.84   32.89
Dominant (nm):             N/A     575
Complementary (nm):        522     470
Excitation Purity:       0.132   0.216
```

```
Illuminant:  WHITE          Angle:         0.0 (deg)
Medium:      AIR            Reference:     550.0 (nm)
Substrate:   AIR            Polarization:  Ave ——
Exit:        AIR
Detector:    IDEAL
```

Figure 5-A-5-E : Show 1931 CIE chromatic diagram of pure and doped SiO_3 thin film doped with various Co impurity ratios (1,3,5 and 7%).

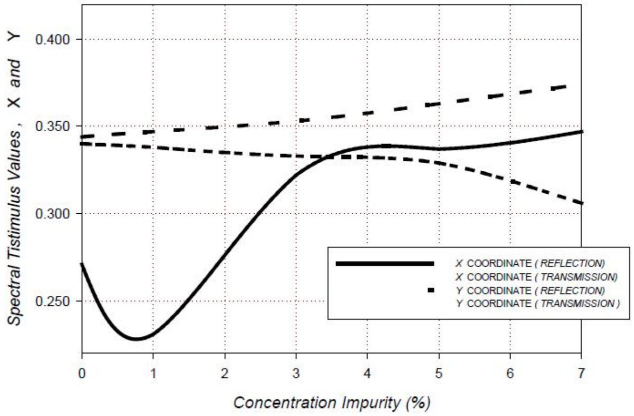


Figure 6 : Spectral tristimulus values *vs*. impurity concentration ratios.

The color coordinates due to light reflected and transmitted by the coating and its variation appears in the Figure as *two small squares*, the excitation purity, dominant and complemtarty wavelength also shown on the same figure. The reflectance profile also shown to the right of figure in each case The variation of *x,y* tristimuls coordinates vs. impurity ratios were shown in Figure 6 and the results were summarized in TABLE 1.

CONCLUSION

From results we conclude that thin film color sensitivity method can be generalized to estimate both film thickness and ratios of adding impurity. The slight changes in impurity create major shifts in their perceived color simply observed on the *xy*-chromatic diagram that show the transition between colors very accurately.

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