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## Color space chromaticity diagram: Estimation of Co impurity ratios in SnO<sub>2</sub> 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° field of view were selected to study color sensation and color matching of SnO<sub>2</sub> thin film doped with various impurity ratios (1,3,5 and 7%) of Co. Results are displaced as a 1931 CIE chromatic diagram.

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### KEYWORDS

Color science;  
CIE;  
Goldlike coatings;  
Data storage.

### INTRODUCTION

Metal oxide has become widely used in many applications<sup>[1]</sup>. 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<sup>[2-4]</sup>. 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<sup>[5]</sup>.

This color change is caused by variations in the reflectance of the thin dielectric film with wavelength<sup>[6]</sup>. Whilst many reports have considered the colors in thin films. Niyomsoan et al. (2002)<sup>[7]</sup> study the color variation in ZnN 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)<sup>[8]</sup>, 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)<sup>[9]</sup> study the color effects of optical antireflection film irradiated by 60 KeV protons to be used in space optical system. Macleod<sup>[10]</sup> discuss optimal; color stimuli applied to multilayer coatings during

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the plot of chromaticity coordinate and the variation of color as the coating is tilted from normal. Tielly (2011)<sup>[11]</sup> discuss the, the active data storage layer (or layers) on CDs, DVDs, HD-DVDs and Blue-Ray discs is reuêctive. Data is stored by making small dots on the recording layer that have a different reuêctivity to the background. The writing process involves decreasing the reuêctivity and the reading process involves detecting these reuêctivity differences. In this article, we calculate the perceived color variation due to adding impurity to thin film and displaced as *xy*-chromatic diagram.

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*.

**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*(λ) generates three main stimuli in a human eye: red (*r*), green (*g*), and blue (*b*). The relative “strength” of each can be estimated by the integrals.

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

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

Relative response

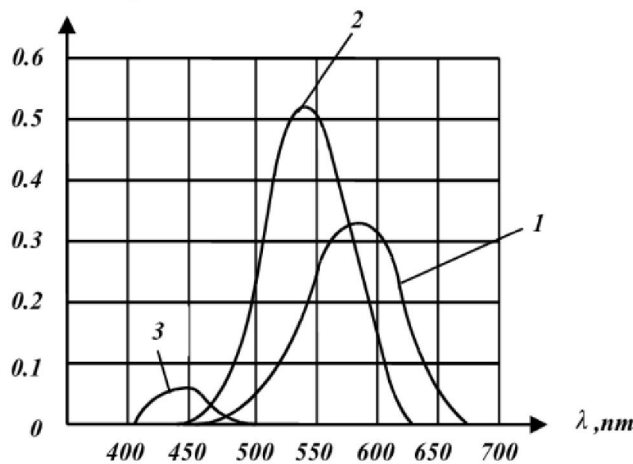


Figure 1 : Relative spectral sensitivity of three kinds of photoreceptors: 1, *R*(λ), cones with erythrolabe; 2, *G*(λ), cones with chlorolabe; 3, *B*(λ), cones with cyanolabe.

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

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

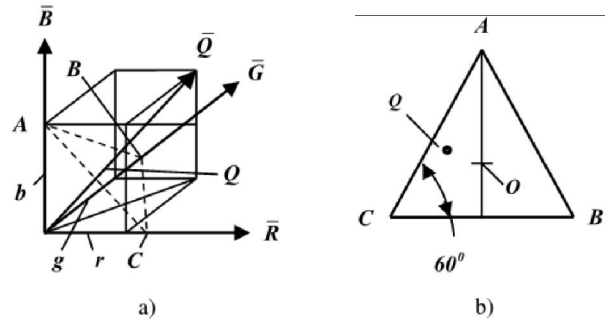


Figure 2 : (a) 3-D color space and (b) its 2-D presentation in a single plane.

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

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

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

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

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

Relative values

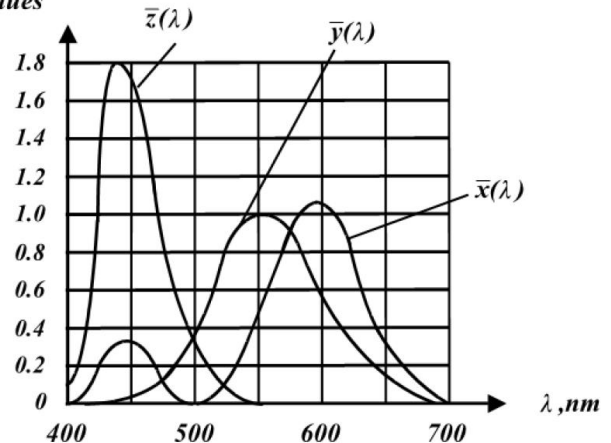


Figure 3 : Color mixture curves (standardized by the CIE)<sup>[11]</sup>.

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:

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

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

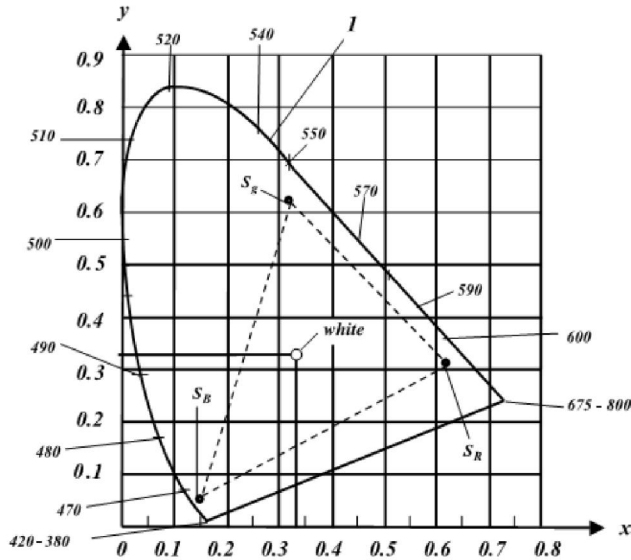


Figure 4 : x, y-diagram of colors (the CIE chromaticity diagram).

## EXPERIMENTAL DETAILS

$\text{SnO}_2$ :Co thin films were obtained by the spray pyrolysis in air atmosphere. A homogeneous solution was prepared by dissolving ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ) and ( $\text{CoCl}_2$ ) 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 ul-

trasonic 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*<sup>[8]</sup>: *First*, the reflected power as a function of wavelength is calculated, this can be done using a standard thin film matrix approach<sup>[6]</sup>. *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<sup>[8]</sup>, and study film color variation due to impurity ratios by evaluating CIE XYZ parameters. As an example  $\text{SnO}_2$  thin film of ~ 400nm thickness and Co as impurity with 1,3,5 and 7% ratios were selected and deposited using spray pyrolysis 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 ( $2^\circ$ ).

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

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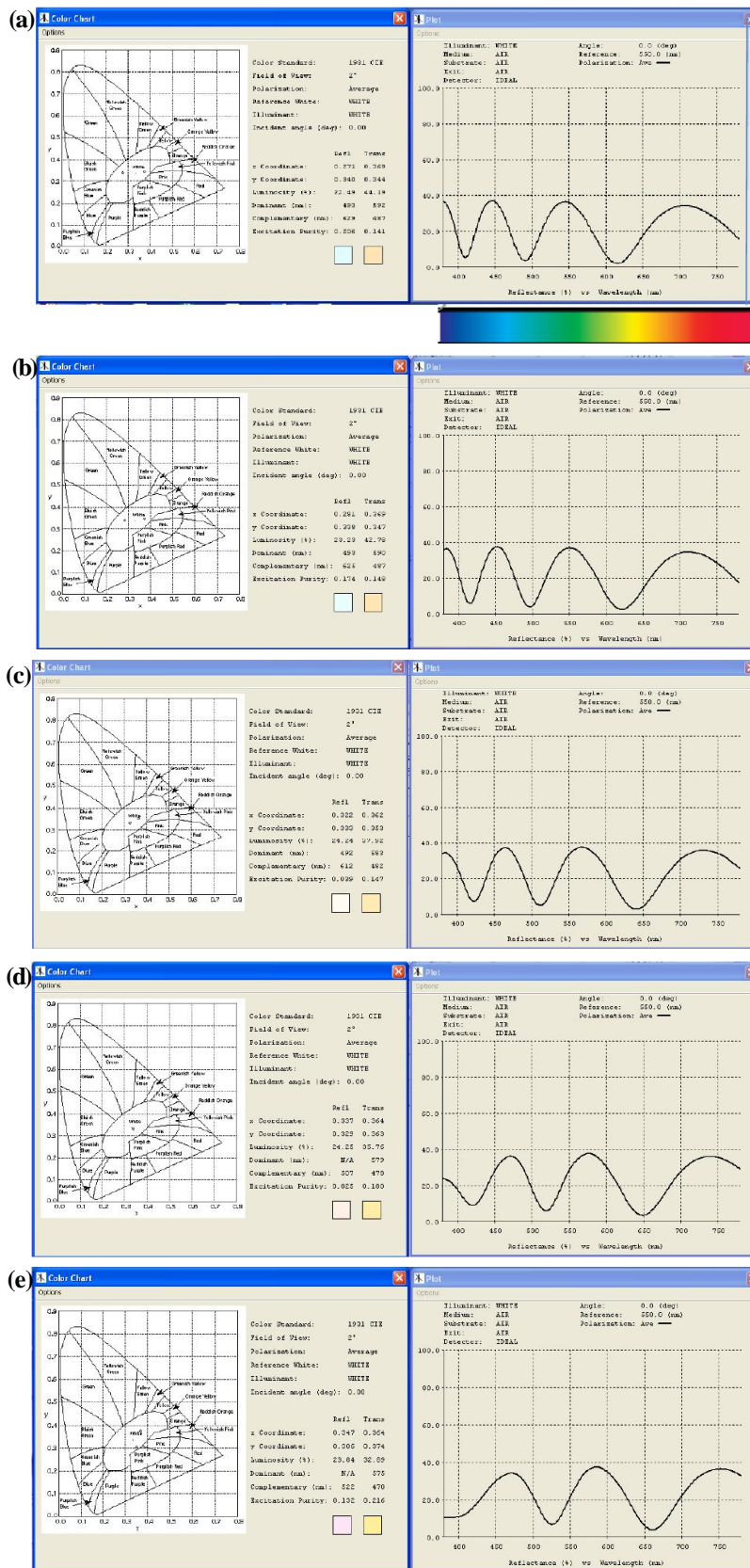
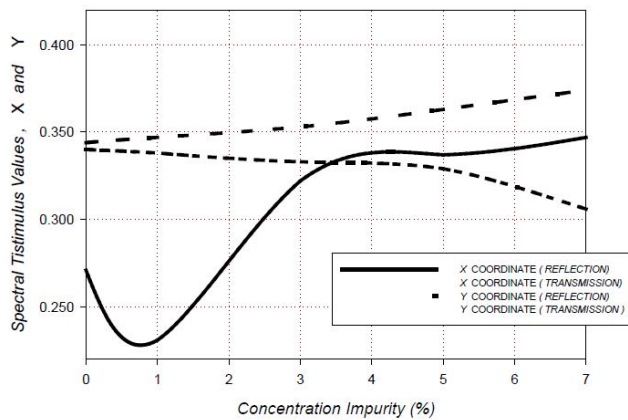


Figure 5-A-5-E : Show 1931 CIE chromatic diagram of pure and doped SiO<sub>2</sub> thin film doped with various Co impurity ratios (1,3,5 and 7%).





**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 complementary wavelength also shown on the same figure. The reflectance profile also shown to the right of figure in each case. The variation of  $x, y$  tristimulus 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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