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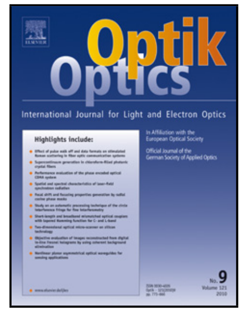


# The Effect of Thin Film Thickness on Thermal Nonlinear Optical Properties and Surface Morphology of Cu Nanostructure Thin Films

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# The Effect of Thin Film Thickness on Thermal Nonlinear Optical Properties and Surface Morphology of Cu Nanostructure Thin Films

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**Abstract**: This study aims to Investigate the effect of thin film thickness on thermal nonlinear optical properties and Surface morphology of Cu Nanostructure Thin Films. Samples are deposited by Thermal Evaporation (TE) and Pulsed Laser Deposition (PLD) Methods. The Morphology of the samples are studied by Field Emission Scanning Electron Microscope (FESEM) images, both samples deposited by PLD and TE showed surface with island nanoparticles. To study the nonlinear optical characteristics of the samples, Z-scan technique was employed. Both TE and PLD samples showed nonlinear absorption and nonlinear refraction. As the thickness of the layers increased, the sign of the nonlinear refraction index changed and the nonlinear absorption coefficient increased.

**Key Words**: Nonlinear optics, Cu thin films, Morphology, Z-Scan technique.

## 1. Introduction

Nanostructured materials have shown attractive properties that are often superior or different to those of their bulk counterparts; such as higher hardness, higher electrical resistivity, soft magnetic properties and nonlinear optical properties [1-3]. Metal nanostructures are among the most studied nanomaterials due to their outstanding size dependent properties. Moreover, solar cells, photovoltaic devices[4, 5], transistors [6] and surface plasmon based analytical devices such as sensors[7-9] are among different applications of metal nanostructured thin films. It has been shown that optical properties of Cu nanoparticles deposited on glass depends strongly on the morphology of thin film[10, 11].

Different experiments are carried out for estimating nonlinear optical properties, such as nonlinear interferometry[12, 13], degenerate four wave mixing[14], nearly degenerate three wave mixing[15], beam distortion measurement[16] and moire′ deflectometry[17]. However Z-scan[13, 18] is one of the most used methods because of its simplicity, high sensitivity and the privilege of giving both sign and magnitude of nonlinear absorption coefficient and refractive index.

The aim of this paper is to study the effect of thin film thickness on thermal nonlinear optical properties and surface morphology of Cu nanostructure thin films. For more accurate studies, Samples are prepared by two different methods of, Thermal Evaporation (TE)[19] and Pulsed Laser Deposition(PLD)[20, 21]. Their nonlinear optical characteristics are estimated by Z-scan and the morphology of samples are studied by Field Emission Scanning Electron Microscope (FESEM) images.

## 2. Experiments

### *2.1 Preparation of samples*

In both deposition methods, lamel glasses were used as substrates. In TE method, an Edwards Vacuum Coater-306 was used for depositing Cu thin films in vacuum pressure around $6\times10^{-5}$ Torr. In this condition the mean free path is 1m and evaporated particles can reach the substrate without excessive collisions. The distance between crucible center and substrates was 12cm. Once the desired chamber vacuum is obtained, the electric current passes through the Tungsten crucible in which copper granules are placed. The electric current is increased gradually to avoid dispatching macroscopic particles from Cu granules, the evaporation of Cu granules took place at 100A. Thin films with thicknesses of 25, 130 and 290 nm were deposited during 15, 45 and 90 minutes, respectively.

In PLD process, Cu thin films was prepared by the second harmonic wavelength (532nm) of Nd: YAG pulsed laser with 10Hz repetition rate and 40ns pulse duration. The deposition processes of thin films with thicknesses of 45, 130 and 240nm were performed during 2.63, 7.6 and 14 minutes respectively. The vacuum pressure was approximately $4\times10^{-5}$ Torr.

### *2.2 Analyses*

Surface morphology of the samples is studied by Field Emission Scanning Electron Microscope (FESEM) images which were obtained by a Hitachi S4160 microscope. Thicknesses of the samples were estimated by cross section FESEM. The thickness of TE samples was estimated to be 25, 130 and 290 nm. The PLD samples are also estimated to be at the same order of thickness 45, 130 and 240 nm. Optical absorption spectrum are used for studying optical properties of Cu thin films which were collected in the region 400-800 nm by an AvaSpec-ULS2048L UV-visible spectrometer.

Nonlinear absorption coefficients and refractive indices of the samples were measured by the well-known Z-scan experiment (Fig.1) using a CW diode laser with output power of 130mw and wavelength of 532nm and the focal length of the lens was 21cm.

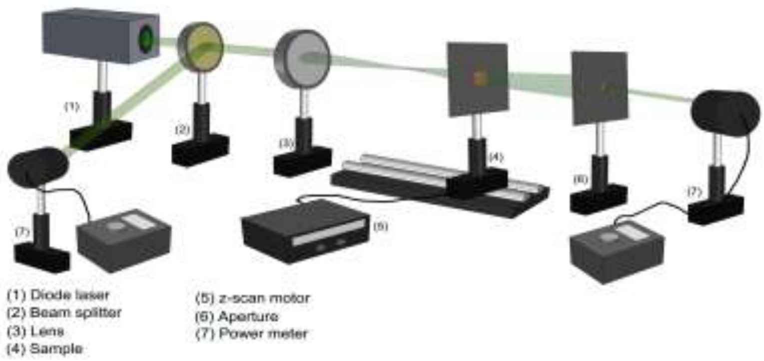


Fig.1. closed aperture Z-scan experimental setup.

## 3. Results and discussions

### *3.1 Surface Morphology*

FESEM images of TE Cu thin films are presented in (Fig.2). Discrete nanoparticles can be observed in samples of 25 and 130nm thickness, while in sample of 290nm, it seems that the void between nanoparticles shaped at the early stages of the deposition process is filled and a semi-continuous film is formed. FESEM images of PLD Cu thin films (Fig.3) also shows formation of discrete nanoparticles, and as we can see the PLD Cu thin film of 240nm thickness deposited during 14 minutes had discrete nano-islands too, and didn't form any semi-continuous film.

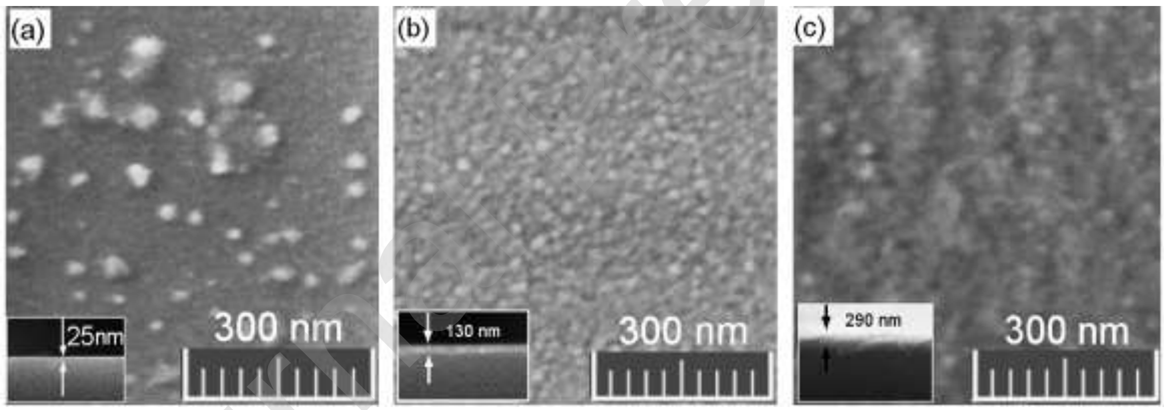


Fig.2. FESEM images of TE Cu thin films with different thicknesses; (a) 25nm, (b) 130nm and (c) 290nm.

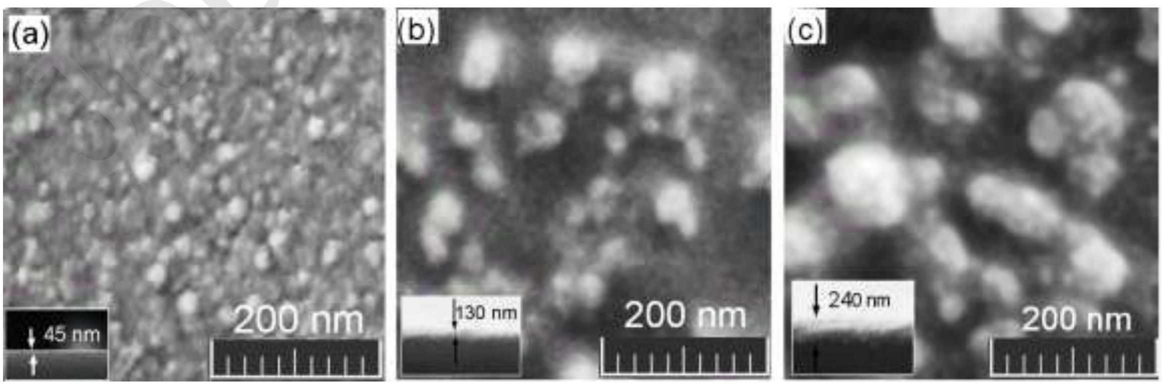


Fig.3. FESEM images of PLD Cu thin films with different thicknesses; (a) 45nm, (b) 130nm and (c) 240nm.

### *3.2 UV-VIS spectra*

We used the UV-VIS spectroscopy to determine the linear characteristics of the thin films. The results obtained from the UV-VIS spectroscopy in Fig.4, show that samples have plasmonic absorption peaks at visible region. The results are represented in Table.1.

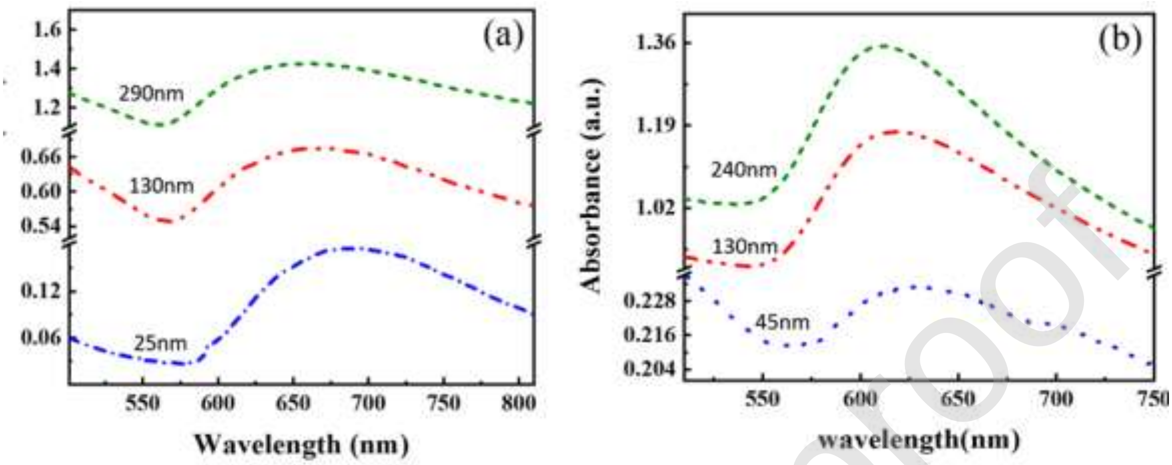


Fig.4. Optical Absorption spectra of (a) TE and (b) PLD Cu thin films with different thicknesses.

**Table.1. Results for Optical Absorption spectra of Cu Nano Structure thin films.**

| Sample | Thicknesses (nm) | Plasmonic absorption peak (nm) |
|---|---|---|
| TE | 25 | 695 |
| | 130 | 623 |
| | 290 | 651 |
| PLD | 45 | 611 |
| | 130 | 596 |
| | 240 | 616 |

### *3.3 Nonlinear Optical Properties*

Closed aperture Z-scan curves for PLD and TE samples are shown in Figs.6 had interesting results, TE and PLD samples with 25 and 45 nm thickness shows a valley–peak configuration indicating positive nonlinear refractive index and self-focusing effect. But, Z-scan curves for 130nm Cu thin films synthesized by both TE and PLD shows a peak–valley behavior, related to negative nonlinear refractive response. As we know thermal nonlinearity originates from refractive index variations due to changes in temperature (dn/dT). In the case of gases, dn/dT is negative because as temperature increases their density decreases, while for condensed matter it may be either positive or negative depending on material structure[22]. So due to changing of surface morphology and the particles sizes by increasing the thickness, the results are reasonable.

Cu thin films of 290 nm thickness synthesized by TE, indicates no nonlinear refraction response, as with an increase in the deposition time, copper nanoparticles are placed so close to each other that there is no void between them. Cu thin films of 240 nm thickness synthesized by PLD indicates no nonlinear refraction response too, as with an increase in the deposition time, Copper particles have large sizes and they formed larger clusters on the substrate. Hence, with high thermal conductivity of copper, the temperature difference between center and edges of the gaussian laser beam which leads to the self- focusing or defocusing effect (d*n*/d*T*), will vanish. Increase in transmittance near focal plane is associated with saturation of the single photon absorption of Cu nanoparticles.

Nonlinear refraction index ($n_2$) can be estimated from the Z-scan data using the peak-valley transmittance difference [13]:

$$\Delta T_{pv} \cong 0.406|\Delta\varphi_0| \qquad (1)$$

Where $\Delta\varphi_0 = k\Delta n_0 L_{eff}$ is the on-axis phase shift at the focus, $L_{eff} = (1 - e^{-\alpha L})/\alpha$ , α is the linear absorption coefficient and L is the sample thickness. Here $\Delta n_0 = n_2 I_0$ and $I_0$ is on-axis intensity at the focus. The results are shown in Table2. As thickness increases, the magnitude of $n_2$ increases and the sign changes in both TE and PLD samples.

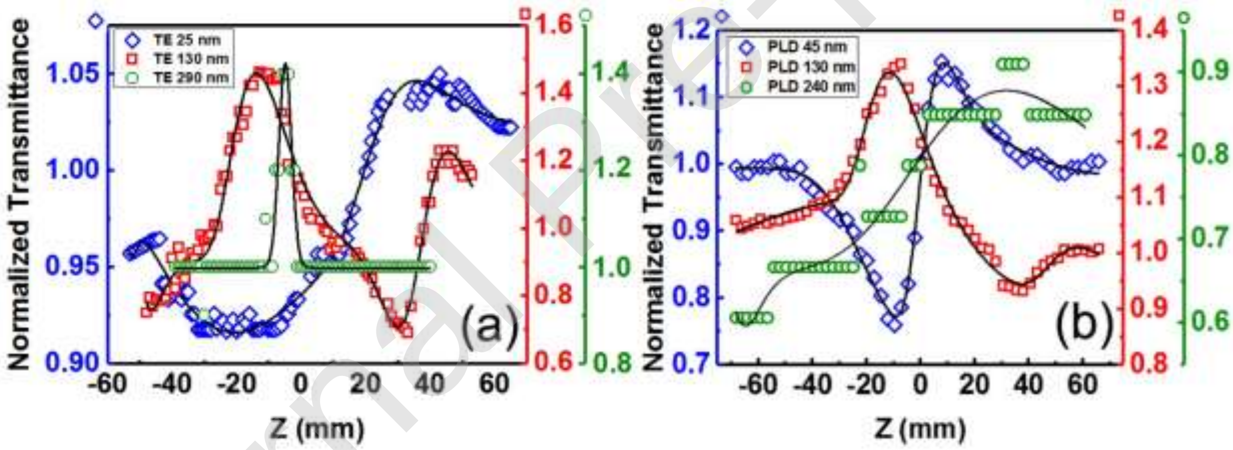


Fig.6. Closed aperture Z-scan curves for Cu thin films prepared by (a) TE and (b) PLD deposition methods

Open aperture Z-scan curves for Cu thin films prepared by TE and PLD are shown in Fig.7. All PLD and TE samples present nonlinear absorption coefficient with negative sign related to the saturation of single photon absorption.

In Z-scan open aperture experiment β can be obtained by the normalized transmittance[13]:

$$T(z) = \sum_{m=0}^{\infty} [-q_0(z.0)]^m/(m+1)^{\frac{3}{2}} \qquad (2)$$

where

$$q_0(z.t) = \beta I_0 L_{eff}/(1 + z^2/z_0^2) \qquad (3)$$

and $z$ is the sample position with respect to focal point and $z_0$ is Rayleigh length. Results are represented in Table2. Nonlinear absorption coefficient of the TE samples are decreased with increasing thickness of thin films, which is expected since in equation (3) $\beta$ and $L_{eff}$ are in inverse proportion.

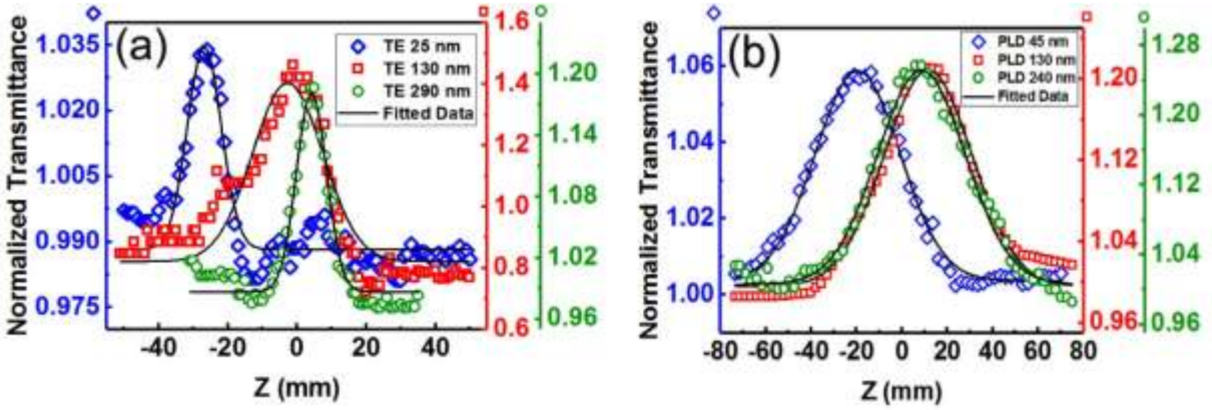


Fig.7. Open aperture Z-scan curves for Cu thin films prepared by (a) TE and (b) PLD deposition methods.

**Table 2. Results for nonlinear characteristics of Cu/glass thin films estimated by Z-scan experiments.**

| sample | Thicknesses (nm) | $n_2$ ($cm^2/W$) | β (cm/W) |
|---|---|---|---|
| TE | 25 | $3.16\times10^{-4}$ | -73.2 |
| | 130 | $-8.34\times10^{-4}$ | -38.8 |
| | 290 | — | -30.1 |
| PLD | 45 | $4.33\times10^{-4}$ | -65.9 |
| | 130 | $-5.36\times10^{-4}$ | -43.4 |
| | 240 | — | -38.2 |

## 4. Conclusion

The effect of thin film thickness on thermal nonlinear optical properties and surface morphology of Cu nanostructure thin films was studied. It was found that the Cu/glass thin films deposited by TE had discrete surface structure. Island nanoparticles can be observed in samples of 25 and 130nm thickness, while in sample of 290nm, it seems that a semi-continuous film is formed. PLD Cu thin films of 45 and 130 nm thickness also shows formation of discrete nanoparticles. The PLD Cu thin film of 240nm thickness has discrete large nano-islands.

Cu/glass thin films deposited by PLD and TE with discrete nanoparticles shows both thermal nonlinear refraction and nonlinear absorption; whereas the TE Cu thin film of 290nm thickness and PLD Cu thin film of 240nm thickness only illustrated nonlinear absorption. In both methods, Cu thin films with higher thicknesses shows higher magnitude of thermal nonlinear refraction index and the sign is changing. Magnitude of nonlinear absorption coefficient of the both TE and PLD samples decreased with increasing film thickness.

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