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Humidity Sensing Properties of CdS Nanoparticles Synthesized by Chemical Bath Deposition Method

Ramazan Demir,[†,‡] Salih Okur,[*,§] Mavişe Şeker,[§] and Muhsin Zor[†]

[†]Department of Physics, Faculty of Science, Anadolu University, Eskisehir, 26470, Turkey

[‡]Canakkale Onsekiz Mart University, Faculty of Science and Art, Department of Physics, Canakkale, 17100, Turkey

[§]Department of Physics, Faculty of Science, Izmir Institute of Technology, Urla, Izmir, Turkey

ABSTRACT: Thin films of CdS nanoparticles were synthesized by the chemical bath deposition (CBD) technique to investigate humidity response characteristics. The morphology and the crystal structure of CdS thin films were investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The quartz crystal microbalance (QCM) technique was used to measure the water vapor adsorption and desorption rates of CdS thin films. The dynamic Langmuir model was used to analyze the kinetics of the moisture adsorption and desorption process under relative humidity (RH) between 17 and 85% RH. Our results indicate that CdS thin films have a great affinity to humidity at room temperature.

1. INTRODUCTION

Cadmium sulfide (CdS), with a band gap energy of 2.42 eV, belongs to the II−VI compound family,[1,2] and there have been a considerable number of studies focused on the development of CdS solar cells[3,4] due to its high absorption coefficient, low cost, and stability.[5,6] Various methods have been used to produce CdS films such as vacuum thermal evaporation,[7] chemical vapor deposition,[8] sol−gel chemical solution growth,[9] ultrasonic spray pyrolysis (USP),[10] rf sputtering,[11] screen printing−sintering technique,[6] and chemical bath deposition (CBD)[12,13] for electro-optical device applications. Among these deposition methods, CBD technique is one of the least expensive and simplest methods, which makes it very attractive to obtain reproducible and uniform CdS films.[14] On the other hand, the presence of moisture is an important parameter for degradation on the conversion efficiency and lifetime of CdS solar cells.[15] Therefore, the effect of the humidity level should be considered during the lamination process.[16]

The quartz crystal microbalance (QCM) technique is a powerful method and is very sensitive to mass changes on the nanogram scale (~1 ng/cm^2) by measuring the change in the resonance frequency. It responds to a given increase of mass simultaneously, regardless of the species deposited.[17,18] It has been frequently used for humidity sensing applications for various materials.[19]

In this work, the CBD technique has been used to fabricate CdS films. The morphology and the crystal structure of CdS thin films were investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The QCM results show that CdS nanoparticles are extremely sensitive to relative humidity changes. Here, we focus only on the moisture adsorption and desorption kinetics of CdS nanoparticles, not on the effect of humidity on CdS solar cell device parameters.

2. EXPERIMENTAL SECTION

2.1. Synthesis of CdS Thin Films. The CBD technique was used to synthesize CdS nanoparticles through ionic reactions between Cd and S ions in alkaline solution prepared in the stoichiometry.[20] To synthesize CdS nanoparticles, 0.2 M alkaline cadmium salt ($CdCl_2H_2O$) solution and 0.48 M thiourea ($CS(NH_2)_2$) solution were prepared. The pH level in the solution was kept fixed at 11.50 with 53.49 M NH_3/NH_4Cl buffer solution. The solutions and deionized water were stirred in the beaker at the constant reaction temperature of 85 °C. Typical chemical reaction steps in CBD technique to obtain CdS nanoparticles are given as follows:

$$CdCl_2H_2O \xrightarrow{H_2O} Cd^{2+} + 2Cl^- + H_2O \quad (1)$$

$$Cd^{2+} + 4NH_3 \rightarrow Cd(NH_3)_4{}^{2+} \quad (2)$$

$$CS(NH_2)_2 + OH^- \rightarrow CH_2N_2 + H_2O + HS^- \quad (3)$$

$$HS^- + OH^- \rightarrow S^{2-} + H_2O \quad (4)$$

$$Cd(NH_3)_4{}^{2+} + S^{2-} \leftrightarrow CdS + 4NH_3 \quad (5)$$

For QCM humidity measurements, gold coated quartz crystal substrates were cleaned in acetone, ethanol, and 2-propanol by use of ultrasonic cleaner for 15 min in sequence, and then rinsed with deionized water. Finally, they were dried at 50 °C on a hotplate. The cleaned gold coated QCM electrodes were immersed in the reaction solution and kept there for 60 min to obtain the desired film. The CdS thin films were dried in a desiccator for 1 day before humidity measurements. The film thickness was determined with a Dektak profilometer from Veeco and found to be around 200 nm.

2.2. Structural Characterization of CdS Thin Films. The surface morphology and crystal structure of the synthesized CdS

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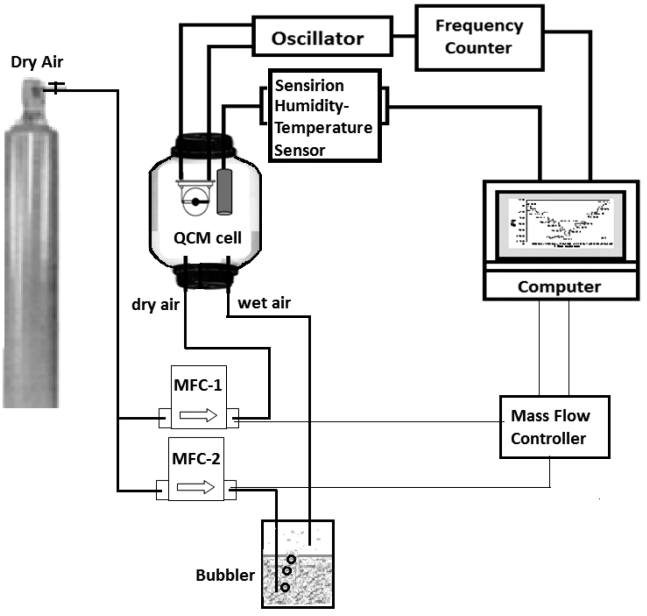

Figure 1. Experimental setup to measure the adsorption and desorption kinetics of CdS thin films under various relative humidity conditions between 17 and 85% RH.

thin films were examined with a scanning electron microscope (Philips XL-30SFEG) and XRD was measured with a Philips X'Pert Pro under Cu Kα radiation.

2.3. Humidity Measurements Using QCM Technique. The QCM technique was used to determine the mass changes due to moist molecules with a resolution of ~1 ng/cm^2. QCM consists of a quartz disk with 0.196 cm^2 area between two gold coated electrodes. The mass change (Δm) on the surface of the quartz crystal was calculated with the Sauerbrey linear frequency change relation[21] as follows:

$$\Delta f = -\frac{2f_0{}^2\Delta m}{A\sqrt{\mu\rho}} \qquad (6)$$

where f_0 is the resonant frequency of the fundamental mode of the QCM crystal, A is the area of the gold coated electrodes on the quartz crystal, ρ is the density, and μ is the shear modulus of the quartz substrate.

A QCM with the Model CHI400A series from CH Instruments (Austin, TX, USA) was used to measure the change in the resonance frequency due to mass loading of water molecules after exposure of the QCM electrodes to various relative humidity levels between 17 and 85%. The QCM was connected via a USB interface to a computer. QCM electrodes used in our study are made of AT-cut piezoelectric quartz crystal with oscillation frequencies between 7.995 and 7.950 MHz. The density (ρ) of the crystal is 2.684 g/cm^3, and the shear modulus (μ) of quartz is 2.947 × 10^{11} g/cm s^2. A change of 1 Hz in QCM resonance frequency corresponds to 1.34 ng of materials adsorbed onto the crystal surface of an area of 0.196 cm^2.

Figure 1 shows the experimental setup to investigate the adsorption and desorption kinetics of CdS thin films under various relative humidity (RH) levels between 17 and 85% RH at room temperature.

The relative humidity on a 100 cm^3 QCM cell was varied between 17 and 85% by controlling the ratio of wet/dry air flow between 0 and 100% with 10 steps using a flow-meter system with Model MKS 647C. The measurements were taken using a hybrid system of a QCM sensor and a commercial Sensirion humidity sensor. The sensor has EI-1050 selectable digital relative humidity and temperature sensors with a response time of 4 s. The humidity sensor was connected to a PC using a Labview program to collect data via the USB port controlled by a U12 ADC system combined with a single chip sensor module (SHT11) (Sensirion, Switzerland).

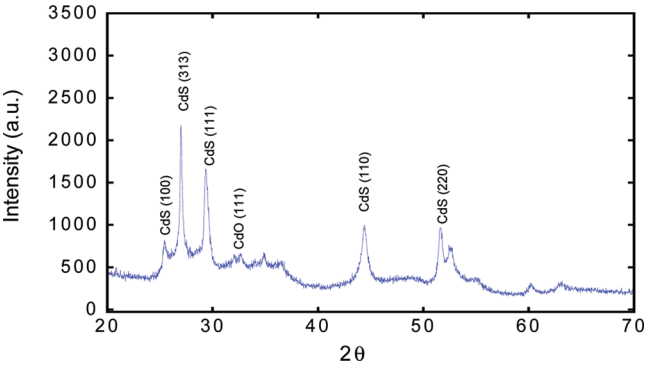

Figure 2. XRD pattern of the CdS nanoparticles.

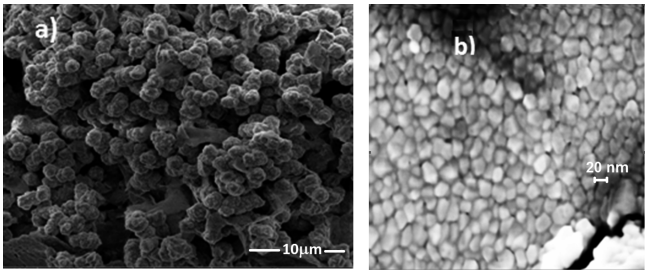

Figure 3. SEM images of CdS nanoparticles.

3. RESULTS AND DISCUSSION

3.1. Structure of CdS Nanoparticles. Figure 2 shows the XRD pattern (taken with a Cu Kα source) of the synthesized CdS nanostructures using the CBD method. Diffraction peaks in the XRD pattern are indexed as orthorhombic. The main peak at the 2θ = 26.9° belongs to the reflection from the 313 plane of CdS nanoparticles. The crystal grain size was estimated as 32.7 nm with the well-known Debye−Scherer equation.[22]

Figure 3 shows the SEM images of CdS films at different magnifications. The SEM image given in Figure 3a shows a porous structure with agglomerated nanoparticles. Those aggregates are clearly seen with 500000× magnification in Figure 3b. The size of CdS nanoparticles can be estimated between 30 and 40 nm compared with the 20 nm scale bar given in Figure 3b.

3.2. QCM Results. Figure 4 shows the adsorption−desorption cycles of a CdS coated QCM sensor compared with relative humidity (RH) values simultaneously measured with a Sensirion commercial RH sensor between 17 and 85% RH for 640 min. The negative QCM resonance frequency response is proportional to the mass change on the QCM sensor due to adsorption and desorption as a result of change in the concentration of moist molecules by varying the relative humidity as shown in Figure 1. The negative frequency response (red circles) is given on the left

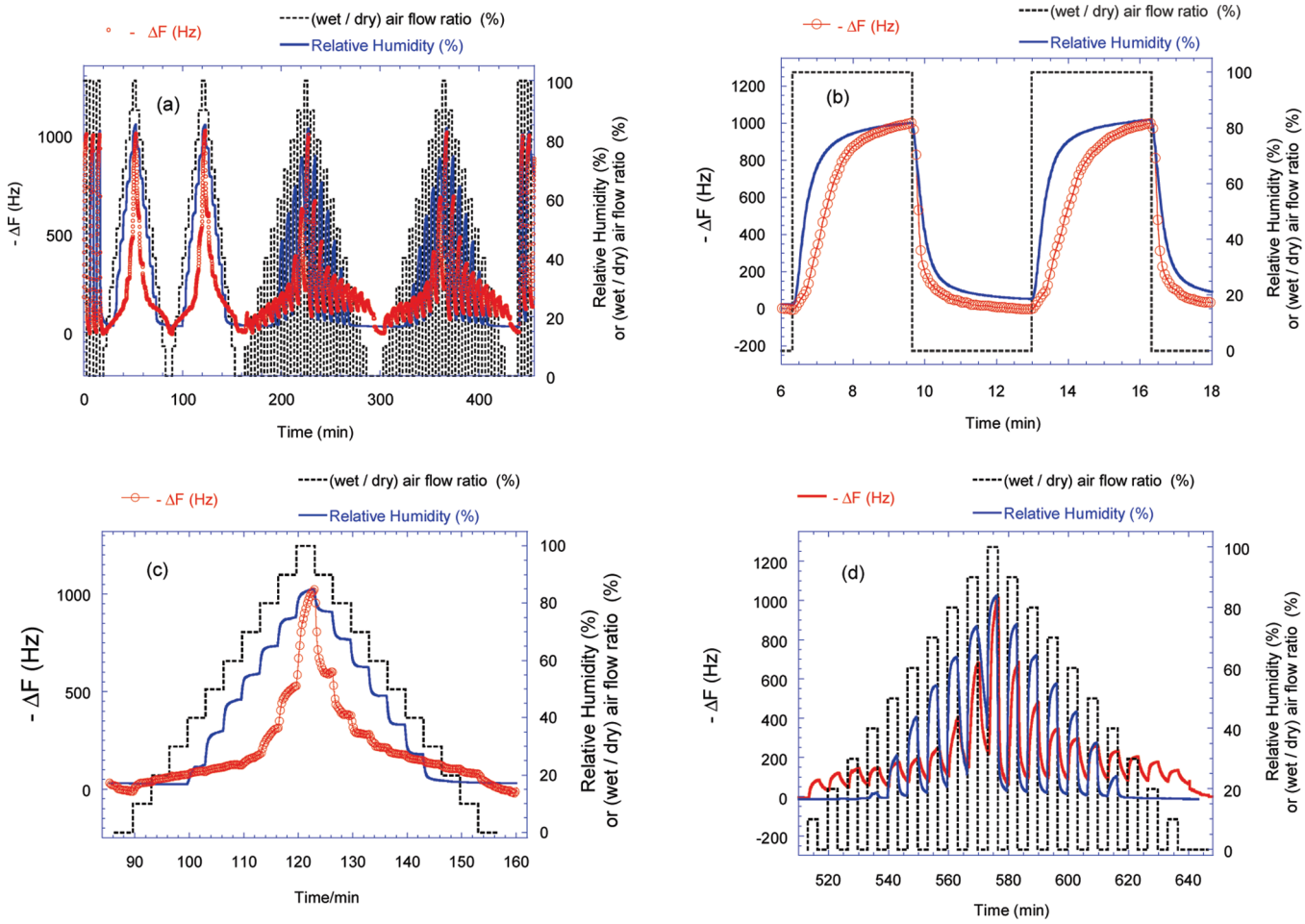

Figure 4. Adsorption and desorption cycles of a CdS coated QCM sensor compared with relative humidity (RH) values simultaneously measured with a Sensirion commercial RH sensor between 17 and 85% RH for 640 min.

sides of the plots, while both the ratio of wet/dry air flow (black dashed line) and the corresponding relative humidity (blue continuous line) are presented on the right sides of the plots in Figure 4. Three types of adsorption and desorption cycles are zoomed out in Figure 4b−d to observe the repeatability and sensitivity of CdS coated QCM sensors against relative humidity changes. The commercial humidity sensor shows 17% RH when 1000 sccm dry air is sent through the QCM cell, while it shows 85% RH with 1000 sccm wet air (by passing dry air through a bubbler half-filled with water kept at a constant temperature of 30 °C). Figure 4b shows two QCM and RH sensor responses when sent only dry and wet air consecutively in 200 s periods to observe maximum adsorption and desorption behaviors. The negative QCM frequency response shows a maximum around 1000 Hz, when 100% wet air with 1000 sccm is sent at 85% RH measured with the Sensirion humidity sensor. The QCM frequency counter is set to 0 Hz as the starting point for the minimum relative humidity at 17% RH, when fully dry air with 1000 sccm is sent through the QCM cell.

Figure 4c shows long time (around 60 min) adsorption and desorption responses of CdS loaded QCM sensors. For this purpose, the wet/dry air ratio is increased in 10% steps for each 200 s period. The QCM frequency response shows two distinct behaviors below and above 30% RH during adsorption. It increases linearly up to 30% RH with a smaller slope and then shows a steep slope for larger RH values. A similar response (frequency drops) is seen below and above 40% RH during the desorption process (in low moisture concentrations). This is a result of hysteresis effect due to different adsorption and desorption kinetics. The QCM sensor loaded with CdS nanoparticles starts to respond in a lower wet/dry air flow ratio (at 10%) compared to the Sensirion RH sensor (at 17%).

Figure 4d shows the short time (6 min) adsorption and desorption responses of CdS loaded QCM sensors. In this case, the wet/dry air flow ratio is also increased by 100 sccm for each 200 s period, while after each adsorption process with a wet/dry air flow step the maximum desorption process is applied by sending maximum dry air with 1000 sccm. Similar low and high responses of the CdS QCM sensor due to hysteresis effect are observed below and above 30% RH with increasing relative humidity from 17 to 85% RH, and below and above 40% RH with decreasing relative humidity from 85 to 17% RH. The hysteresis effect is larger compared to stepwise relative humidity changes between 17 and 85% RH.

Figure 5 shows the CdS QCM sensor response for varying wet/dry air flow ratio between 0 and 100% (Figure 5a) and corresponding relative humidity between 17 and 85% RH (Figure 5b). The hysteresis effect for the short time (6 min) response of CdS coated QCM sensor is larger compared to its long time response (60 min) for relative humidity changes as seen from Figure 5a and 5b.

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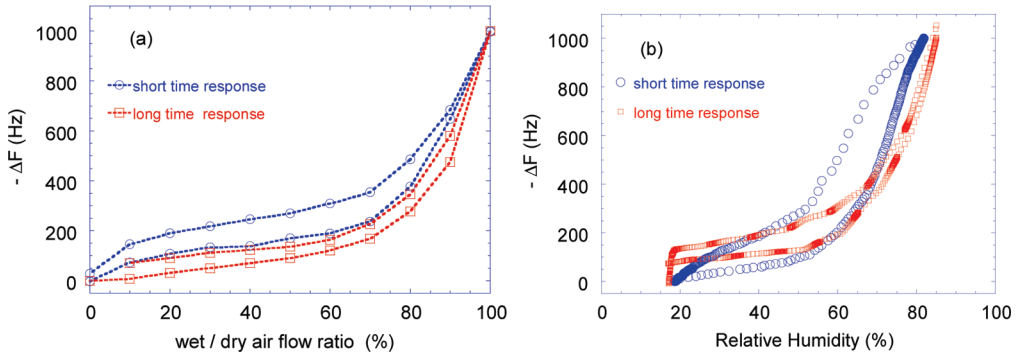

Figure 5. CdS QCM sensor response versus varying wet/dry air flow ratio between 0 and 100% (a) and versus relative humidity between 17 and 85% RH (b).

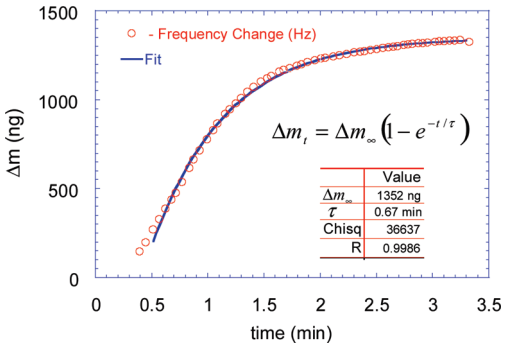

Figure 6. Least-squares fit (solid line) to the Langmuir adsorption isotherm model given in eq 9 for the adsorbed water mass into the CdS films under relative humidities between 17 and 85% RH.

The QCM results show that the CdS nanoparticles are very sensitive to humidity changes and give reproducible adsorption and desorption kinetic behaviors for short time periods. The CdS nanoparticles on QCM respond like a commercial RH sensor and can be used for potential humidity sensor application. The adsorption and desorption kinetic parameters can be obtained using Langmuir analysis.

3.3. Theoretical Analysis of QCM Results Using Modified Langmuir Model. The Langmuir adsorption isotherm model is frequently used to analyze adsorption data to explain the adsorption−desorption kinetics of gas molecules in the literature.[20,21] The relationship between the surface adsorption and desorption rates and the QCM frequency shift (Δf) can be expressed as follows:

$$\frac{d\Delta f}{dt} = (\Delta f_{max} - \Delta f)k_a C - k_d \Delta f \quad (7)$$

where Δf_{max} is the maximum frequency change at the maximum humidity range, C is the concentration of the adsorbed gas, and k_a and k_d are the adsorption and desorption rates, respectively. Integration of eq 7 leads to the solution of the first order differential equation as follows:[23]

$$\Delta f(t) = \Delta f_{max} K'(1 - e^{-k_{obs}t}) \quad (8)$$

where K' is the association constant and k_{obs} is the inverse of the relaxation time. The change in the mass due to moisture adsorption can be fitted to the Langmuir adsorption isotherm model, since the frequency shift is directly proportional to the change of the absorbed mass according to the Sauerbrey relation given in eq 6. One hertz of frequency change corresponds to the increase in the absorbed mass of 1.34 ng on the QCM electrodes.[21] The time dependence of the amount of absorbed water molecules on the film surface Δm_t can be defined as[17,24]

$$\Delta m_t = \Delta m_\infty (1 - e^{-t/\tau}) \quad (9)$$

where $\tau^{-1} = k_a$[water vapor molecules] $+ k_d$; Δm_∞ is the maximum adsorbed mass of the moist molecules on the surface for very long times, when $t \rightarrow \infty$, and it is calculated as 1352 ng.

Figure 6 shows the least-squares fit (solid line) using the Langmuir adsorption isotherm model given in eq 9 for the adsorption parts of the data between 17 and 85% RH given in Figure 4b. The relaxation time τ is obtained as 0.67 min. The average values of adsorption and desorption rates (k_a and k_d) between 17% RH (concentration of 1.18×10^{-4} M) and 85% RH (concentration of 8.06×10^{-4} M) were calculated as 1852 M^{-1} s^{-1} and 0.0127 s^{-1}, respectively.

The corresponding Gibbs free energy ΔG of the adsorption/desorption process at a constant temperature can be obtained with $\Delta G = -RT \ln K_{eq}$, where K_{eq} is the equilibrium constant ($K_{eq} = k_a/k_d$), R is the universal gas constant, and T is the temperature (at 300 K).[25] The equilibrium constant K_{eq} and Gibbs free energy values were 145 700 and −11.89 kJ/mol for the adsorbed water mass between 17 and 85% RH, respectively. The Gibbs free energy with negative sign shows that there is an energy loss for water molecules on CdS thin film surface during the adsorption process. The process is reversible with the hysteresis effect as a result of physisorption via van der Waals forces between two instantaneously induced dipoles (so-called London dispersion force)[26] between adsorbed moist molecules and image charges in the polarized CdS nanoparticles. The QCM results show that CdS thin films are extremely sensitive to humidity changes even for short time (6 min) intervals at room temperature. The effect of moist environmental conditions should be considered for CdS solar cells applications during the lamination process.

4. CONCLUSION

The quartz crystal microbalance (QCM) technique was used to analyze the water vapor adsorption and desorption kinetics of CdS thin films synthesized with the CBD technique. The moisture adsorption rate, moisture desorption rate, and Gibbs free energy kinetic parameters were obtained by using the dynamic Langmuir model under relative humidity (RH) between 17 and 85% as 1852 M^{-1} s^{-1}, 0.0127 s^{-1}, and −11.89 kJ/mol,

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respectively. Our QCM results show that CdS thin films are extremely sensitive to humidity changes even for short time (6 min) intervals at room temperature. The effect of moist environmental conditions should be considered for CdS solar cells applications during the lamination process.

AUTHOR INFORMATION

Corresponding Author

*E-mail: salihokur@iyte.edu.tr. Tel.: 00902327507706. Fax: 00902327507707.

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