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Influence of Solution pH and NH_3 Concentration on Some Properties of CuO Thin Films Deposited by Chemical Solution Method

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Abstract: Copper oxide (CuO) thin films were deposited onto glass substrates using Successive Ionic Layer Adsorption and Reaction (SILAR) method. Structural, surface morphology and optical properties of the synthesized films were studied as a function of ammonia's solution concentration and pH. X-ray diffractometer, AFM, UV-V is spectroscopy were used to investigate the structure, morphology and optical properties of the films. All the films had exhibited amorphous structure for the films with NH_3 concentration 30% and pH 10 which would reflect the low crystallinity and polycrystalline monoclinic structure. Morphological studies, generally, revealed that the uniformity of the film surface and the average roughness and RMS decrease with increasing the ammonia concentration and pH solution. Optical parameters such as band gap energy decreases 2.03-1.92 and 2.57-2.28 eV with increasing the concentration of ammonia and pH values, respectively. It was found that the optimum deposition condition of CuO nanostructure films was with solution pH of about 10 and NH_3 concentration of 30%.

Key words: CuO thin film, SILAR, structure and surface morphology, optical band gap, optical properties, roughness

INTRODUCTION

Copper (II) oxide, also known as tenorite or cupric oxide (CuO) is one of the two main copper oxide compounds CuO and Cu_2O which has a preferred monoclinic structure with high electrical conductivity and a p-type transition metal oxide semiconductor (Ooi *et al*., 2014; Wu *et al*., 2006; Gencyilmaz and Taskopru, 2017). It is chemically stabile, abundance in nature, low coast and non-toxic behavior with narrow band gap at ~1.3- 2.1 eV (Gencyilmaz and Taskopru, 2017; Mageshwari and Sathyamoorthy, 2013; Sonia *et al*., 2015). In addition CuO has high optical properties and high solar absorbance and low thermal remittance make it a promising material for solar cells applications (theoretical efficiency being 18%) (Gencyilmaz and Taskopru, 2012; Mageshwari and Sathyamoorthy, 2013; Sonia *et al*., 2015; Dhanasekaran *et al*., 2012, 2013). In recent years CuO films have received a very large attention for its unique properties and used in a wide range of application such as biosensors and gas sensors (Ghosh *et al*., 2000; Jindal *et al*., 2012; Choi and Jang, 2010), photo catalysis (Liu *et al*., 2012), lithium ion batteries (Chen *et al*., 2009), magnetic storage (Gamino *et al*., 2018), photo-electro-chemical cells (Masudy-Panah *et al*., 2016), photovoltaic device and solar cells and capacitors (Luque *et al*., 2005; Anandan *et al*., 2005). To date, micro and nano-scale of the CuO thin films have been prepared and grown using a number of techniques including radio frequency magnetron sputtering (Ghosh *et al*., 2000), dip coating (Dhanasekaran *et al*., 2013), electrochemical (Dhanasekaran *et al*., 2012), spray pyrolysis (Goodarzi and Eshghi, 2018), electrodeposition (Wang *et al*., 2014), pulsed laser deposition (Hu *et al*., 2016), hydrothermal method (Sonia *et al*., 2015), chemical bath deposition CBD (Sultana *et al*., 2017) and SILAR (Bayansal *et al*., 2013). Among those methods, SILAR is a unique method by which thin films of compound semiconductors can be deposited by alternately dipping the substrate into the aqueous solutions containing ions of each component. The deposition parameters in SILAR method such as solution and NH_3 concentrations, pH of the solution, adsorption, reaction, rinsing times and the deposition cycles number are important and play effective roles in the quality and film properties. In this study, the effect of pH values on the structural, optical, morphological and electrical properties of CuO films has been discussed. In this research, the effect of solution pH and ammonia NH_3 concentration on the adsorption and reaction and some physical properties of copper oxide successive layer thin films deposited on glass substrates. Structural, morphological and optical properties of the deposited

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films were investigated as a function of pH and ammonia NH_3 concentration of the solution reaction and choose the optimum deposition condition.

MATERIALS AND METHODS

Experimental part: CuO thin films were synthesized on glass substrates using the SILAR method. The materials and method and the experimental details was reported in (Alkhayatt *et al*., 2018). 0.1 M copper copper (II) chloride dehydrate ($CuCl_2$•$2H_2O$) was dissolve in 100 mL of deionized water. To study the effect of the pH of the solution and ammonia concentration on the growth and properties od CuO films, the pH value of the solution was adjusted to 8, 10, 11.5 by adding an aqueous ammonia (NH_3 30%) whereas to hand the solution pH was adjusted to (10) by adding aqueous ammonia (NH_3) with different concentrations (i.e., 10, 20 and 30%). Then the solution was heated up to 80-90°C during the experiments, the temperature was kept constant at this level. In order to obtain the required thickness for the thin films, 10 cycles of SILAR were applied, the SILAR cycle details also reported by Alkhayatt *et al*. (2018). Finally, all the samples were cleaned in an ultrasonic bath for 10 min in order to detach bigger and tightly bonded particles before the analysis.

The structural, surface morphology and the optical properties of the prepared films were studied using XRD-6000 Shimadzu diffractometer using CuKα radiations (λ 1.5406Å) over the range of 2Θ = 20-70° at an operating voltage and current of 40 keV and 20 mA, respectively, CSPM Model AA3000 AFM and Mega 2100 UV/V is spectrophotometer in the wavelength range 200-1100 nm were used.

RESULTS AND DISCUSSION

Structural studies X-ray diffraction: The XRD patterns of CuO thin film prepared on glass substrates at different ammonia NH_3 concentrations 10, 20 and 30% and at 5 cycles, 20 sec for each cycle and solution pH 10 was shown in Fig. 1. The CuO thin film was found to have amorphous and very low crystallinity structure where there is no appear of a clear peak as shown in the Fig. 1.

This can be attributed to the low number of deposition cycles and unsuitable ammonia concentrations 10 and 20% then when the ammonia concentration be 30% the crystal structure enhanced and two low intensity beaks were appears as shown in Fig. 1. It can be argued that this is the suitable ammonia concentration for depositing CuO thin film by SILAR method. These results were in a good agreement with Gencyilmaz and Taskopru

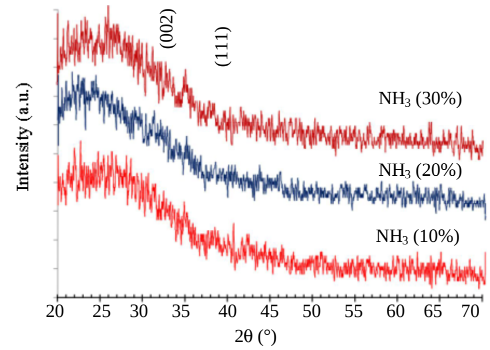

Fig. 1: XRD patterns of the CuO thin films deposited at different ammonia concentration

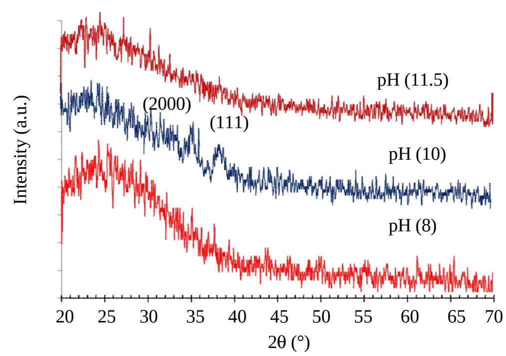

Fig. 2: XRD patterns of the CuO thin films deposited at different pH solution

(2017) and Bayansal *et al.* (2016) where they used NH_3 concentrations 28 and 30%. The diffraction patterns of CuO thin films prepared on glass substrates at solutions pH 8, 10 and 11.5 with 30% ammonia concentration, 10 deposition cycles number and 20 sec as cycle time was shown in Fig. 2. The figure revealed that CuO thin films demonstrated a polycrystalline nature and grown in the monoclinic crystal structure for the deposited films at solution pH 10 only. While for the deposited at solutions pH of 8 and 11.5 the films had amorphous structure. So, it can be conclude that the solution with pH = 10 is a suitable optimum value for the deposition of CuO films. At solution pH 10, the main peaks were appeared at 2Θ = 35.28 and 38.380° which belong to 002 and (111) planes, respectively, it is well matched with the CuO card (JCPDS Card No. 41-0254). These results were similar in their behavior to Bayansal findings (Bayansal *et al*., 2012, 2013; Gencyilmaz and Taskopru, 2017).

Atomic Force Microscope (AFM): Atomic Force Microscopes (AFM) are well suited approach for visualize the surface texture of the deposited CuO thin films, especially when the surface feature sizes are far below

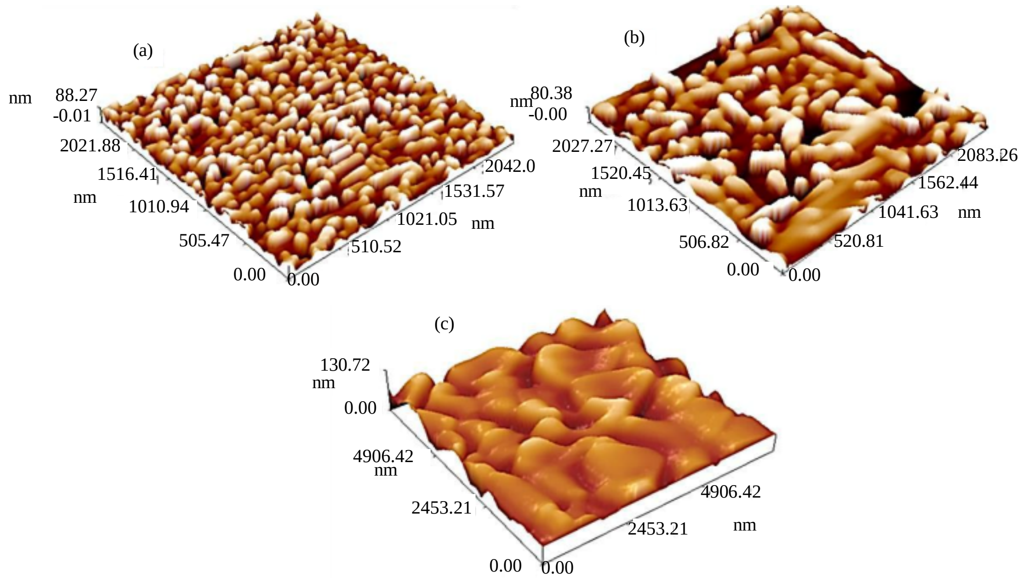

Fig. 3: AFM images of CuO thin films at different NH_3 ammonia concentration; a) 10%; b) 20% and c) 30%

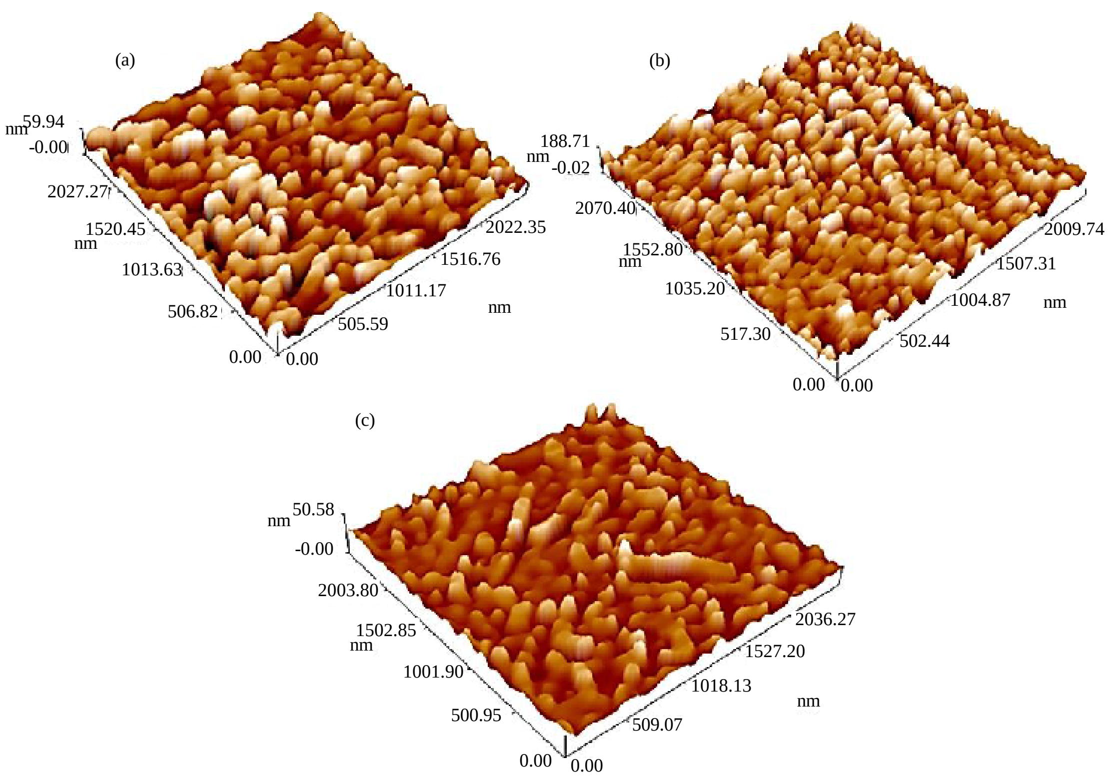

Fig. 4: AFM images of CuO thin films deposited at different pH solution; a) 8; b) 10 and c) 11.5

1 μ. Figure 3 and 4 shows the AFM images of CuO the thin films on glass substrate at different ammonia concentration and pH values of solution, respectively. The obtained results demonstrate that deposited CuO thin films on glass substrate exhibits different surface texture and retrieved from the possibilities on tailoring the surface texture of the CuO thin films by varying ammonia concentration as shown in Fig. 3 and pH solution in

Table 1: The average roughness and root mean square of CuO thin films at different ammonia concentration and pH solution

Parameters/Variables	Average roughness (nm)	Root mean square (nm)	Avg. diameter (nm)
10%	19.20	22.60	92.07
20%	18.30	21.40	126.69
30%	11.30	14.70	166.49
8	9.42	11.60	105.84
10	28.70	35.90	67.35
11.5	4.45	5.62	109.44

Fig. 4. These figures show that the surface of all samples were uniform and homogenous without any cracks. At different ammonia concentration, the average roughness and the measured Root Means Square (RMS) values were decreased with increasing the ammonia concentration were shown in Table 1. The result showed decrease in the average roughness root mean secure of the film surface with the increase of ammonia concentration while the average grain diameter increase up to 166.49 nm for ammonia concentration 10% as shown in the Table, the increase in the grain diameter refer to more grown with suitable of ammonia concentration which leads to get suitable pH and suitable solution for adsorb Cu ions and suitable reaction take place to get CuO structure. These results were in similar in their behavior to that by Gencyilmaz and Taskopru (2017) and Masudy-Panah *et al*. (2016). However, at variable pH values, the AFM images in the Fig. 4 show that the average roughness and the measured Root Means Square (RMS) values were high at pH 10 (28.7), (35.9). The minimum value was noticed at pH 11.5 (4.45), (5.62) but at pH 8 it was place between them (9.42), (11.6) as shown in Table 1. This behavior attributed to unsuitable solution pH values (8 and 11.5) to prepare CuO films and the optimum adsorption and reaction of Cu ions to deposit CuO crystal. These results were agreed with (Bayansal *et al*., 2012, 2013; Mageshwari and Sathyamoorthy, 2013).

The variation of roughness, RMS roughness and the average grain size values clearly indicate that the ammonia concentration and pH solution influence the surface morphology of the deposited films and the quality of the thin film surface can be also controlled by the variation of the these parameters according to the AFM results.

Optical studies: According to the results, ammonia concentration and pH solution had an effect on the growth of CuO films, therefore ,the optical properties must be affected. The optical transmittance spectra of the films as a function of ammonia concentration and pH solution in the wavelength range of 400-1100 nm are shown in Fig. 5 and 6, respectively. At different ammonia concentrations, as shown in Fig. 5, the film had a low average transmittance at about 68% for the deposited film with ammonia concentration of 30%. The film deposited at

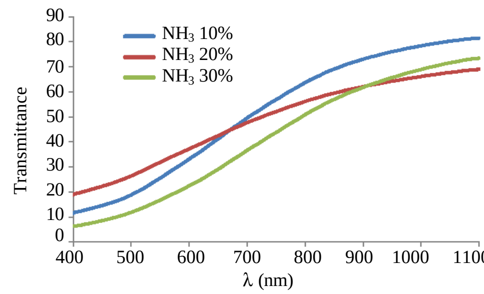

Fig. 5: Optical transmittance spectra of CuO films deposited at different ammonia concentration

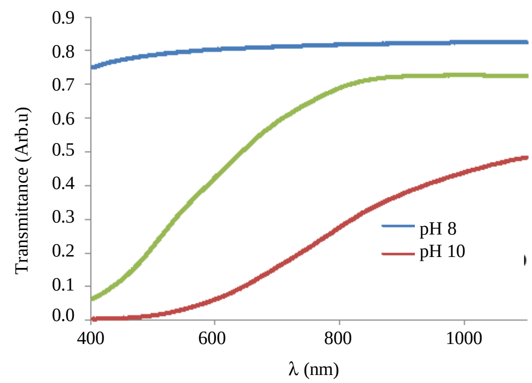

Fig. 6: Optical transmittance spectra of CuO films deposited at different pH solution

NH_3 10% concentration had a highest transmittance (about 80%). It was decreased gradually with increasing ammonia concentration from 10-30% where the deposited rate and thickness of the films was increase with the increase of ammonia concentration (Mageshwari and Sathyamoorthy, 2013). It is found that 30% ammonia concentration is the suitable concentration for deposit CuO films as in XRD results. These results were in similar behavior to Dhanasekaran and Mahalingarm (2012).

On the other hand, at variable pH value as shown in Fig. 6, the film had a low transmittance at about 47% for pH 10. The film which having pH 8 has the about 82% transmittance. The transmittance is decreased gradually with increasing pH value up to 8 then decreased at pH 11.5 (The transmission of the film decreases with increasing the pH, at pH 11.5 which it starts increasing with a further increase in pH), it can also attributed to the increase the thickness of the film with solution pH 10. These results were agreed with (Gencyilmaz and Taskopru, 2017; Mageshwari and Sathyamoorthy, 2013).

For the direct transition gap materials the optical band gap energy E_g was calculated from the absorption

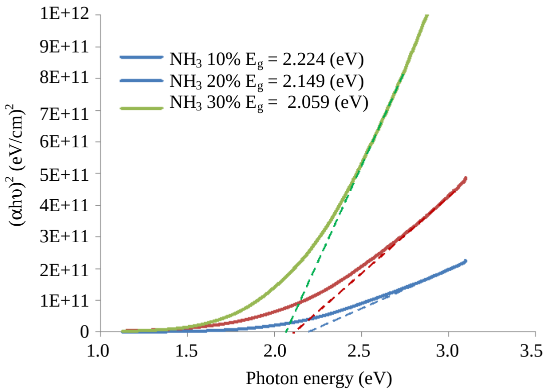

Fig. 7: Variation of $(\alpha h\upsilon)^2$ vs. hυ of CuO thin films deposited at NH_3 10-30% concentrations

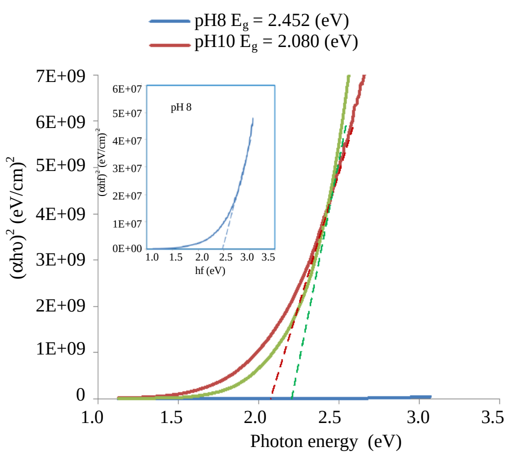

Fig. 8: Variation of $(\alpha h\upsilon)^2$ vs. hυ of CuO thin films deposited at solution pH (8, 10 and11.5)

spectra using the dependence of the absorption coefficient (α) on the photon energy (hυ) by using the Tauc relation (Ramya *et al*., 2015; Alkhayatt and Hussian, 2017):

$$(\alpha h\upsilon) = C(h\upsilon - E_g)^{1/2} \quad (1)$$

where, C is an energy independent constant. Hence, in order to investigate the effect of ammonia concentration and pH solution on the optical band gap, the optical energy gap (E_g) of the prepared films can be obtained by plotting $(\alpha h\upsilon)^2$ versus (hυ) extrapolating the straight line portion of this plot to the energy as in the Fig. 7a-c and Fig. 8a-c, respectively. It was seen that the (E_g) values of the films had a linear dependence on the ammonia concentration and pH solution which means that the increase in the NH_3 and pH may lead to decrease in the energy gap (E_g) values of the CuO thin films for the deposited films as listed in Table 2. The behavior of

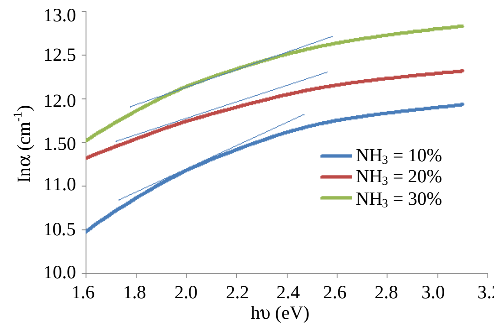

Fig. 9: Variation of ln (α) with energy of CuO thin films with different ammonia concentration. Inset: Urbach energy (E_u) values

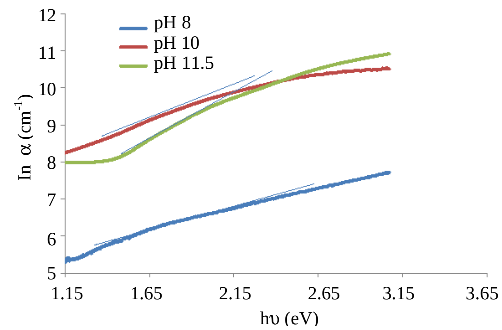

Fig. 10: Variation of ln (α) with energy of CuO thin films with different pH solution. Inset: Urbach energy (E_u) values

decreasing the energy band gap related to the increase in film thickness which creates a localized state in the energy gap higher and lower the valence band and conduction band edges (Bayansal *et al*., 2012, 2013).

In the energies lower than the optical energy gap, there is an absorption tails which is called Urbach energy (E_u) such tails in films are formed mainly by volatility in bond angles and length. In the exponential edge region, Urbach rule is expressed as follow (Urbach, 1953; Lakhdar *et al*., 2014):

$$\alpha = \alpha_o \exp\left(\frac{h\upsilon}{E_u}\right) \quad (2)$$

Where:

α = The absorption coefficient
α_o = Constant
E_u = The Urbach Energy

The Urbach energy values were estimated from the slopes of the plots inset of Fig. 9 and 10. These figures showed and confirmed that the prepared CuO thin films with different ammonia concentration and pH solution,

Table 2: The optical properties of the CuO thin films at different ammonia concentration and pH solution

Parameters/Variables	Thickness (nm)	E_g (eV)	E_u (eV)
10%	58.87	2.224	0.69
20%	76.25	2.149	0.97
30%	88.31	2.095	0.70
8	140.64	2.452	1.00
10	145.50	2.080	0.42
11.5	155.24	2.214	0.44

respectively were satisfied Urbach rule and obey his empirical Eq. 2. This equation describes the optical transition between the occupied levels in the valence band tail and the unoccupied levels of the conduction band edge. The results show that (E_u) increases with the increase of ammonia concentration and pH solution as shown in Table 2 which attribute to the crystallinity of the prepared films as confirmed in the structure properties.

CONCLUSION

CuO thin films were deposited via. successive ionic layer adsorption and reaction SILAR method. The effect of ammonia concentration and pH solution as investigated for the first time. Analysis of the results led to the following conclusions:

The deposited CuO film have polycrystalline nature and grown in monoclinic crystal structure at pH 10 but at pH 8, 11.5 and different ammonia concentration its amorphous. The films had high transmittance at low deposition ammonia concentration and pH solution, it decreased with increasing of them. The optical band gap (E_g) in general decreased with increased ammonia concentration and pH solution and the Urbach energy (E_u) increase with increase NH_3 and pH. The average roughness and the measured Root Means Square (RMS) at the different ammonia concentration and pH solution were decreased. It can be concluded that SILAR method was a suitable method for preparation of CuO films with optimum ammonia 30% concentration and solution pH 10 for optical, optoelectronic and solar cell applications.

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