Effect of pH on chemical bath deposited Nickel selenide (NiSe) thin films.

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Abstract: Thin film of Nickel Selenide (NiSe) was deposited on glass substrate at 303k using chemical bath deposition (CBD) technique. The films were deposited from aqueous solution containing Ni^{2+} and refluxed sodiumselenosuphate (Na_2SeSO_4) at varying pH, volume of concentration of solutions with constant time. The optical absorption data reveals that films of NiSe absorbs strongly at the ultraviolet range of 0.35µm and has above 70% transmittance in the VIS –NIR regions. The results show that the film has energy gap (E_g) of 2.45eV – 2.70eV, thicknesses ranges from 0.05µm – 0.51µm. The film is found suitable as anti- reflection coatings.

Key Words: Nickel Selenide, Chemical bath deposition, pH, thin films.

1.0 INTRODUCTION

In the past years, synthesis and physical characterization of thin film semiconductors have attracted significant interest. They have a wide variety of applications such as solar cells electroluminescent devices, photoconductors, sensor and infrared detector devices (Osuji., 2007). Chemical bath deposition method has been used for the deposition of thin films of sulphides and selenides.

. The basic principal involved in chemical bath deposition technique is the controlled precipitation of the desired compound from a solution of its constituents. This requires that the ionic product must exceed the solubility product. The use of complexing agent is very common in the preparation of thin films. Many researchers use various complexing agents such as sodium citrate, ammonia11, triethanolamine and disodium ethylenediamine tetra-acetate during deposition of thin films (Hankare, 2011).

In the present investigation, thin films of NiSe were prepared from an alkaline bath using $NiCl_2 . 6H_2O$ and refluxed Na_2SeSO_4 acted as a source of nickel and selenide ion, respectively. DisodiumEthylene-diamine tetra-acetate EDTA [$Na_4(C_{10}H_{16}N_2O_8)$] was used as a complexing agent during deposition process. The optical properties of NiSe thin films were determined. Two important factors that should be considered in producing these materials are the band gap energy matching the solar spectrum and the competitiveness of production cost. The rationale for this is that thin films modules are expected to be cheaper to manufacture owing to their reduced material costs, energy costs, handling costs and capital costs. Esparza-Ponze (2009). Nickel selenide is a semiconductor which is suitable for applications in solar cells, sensor and laser materials. Films of nickel selenide have previously been prepared by thermal evaporation and chemical bath deposition(CBD). Sahraei.(2008).

Materials and Method.

Chemicals Used: The reagents used are Nickel Chloride, SodiumSelenoSulphate Na_2SeSO_4, Ammonia Solution $NH_4(OH)$ which helps in adjusting the alkalinity of the solution used . Ethylene Diamine-Tetra Acetate (EDTA) serves as a complexing agent for the deposition of

Nickel Selenide film. Mean while sodium sulphite in aqueous solution was used to reflux Selenium powder to obtain sodium selenosulphate (Na_2SeSO_4). Nickel Selenide (NiSe) was deposited by the reaction of solution containing [Nickel Chloride Dehydrate ($NiCl_2.6H_2O$)].

Film Deposition

The deposition baths were prepared as follows:

1.0ml of 0.1M of DisodiumEthylene-diamine tetra-acetate EDTA [$Na_4(C_{10}H_{16}N_2O_8)$] was added to 3.0ml of 1.0M of $Nicl_2.2H_2O$ in a 100ml beaker.2.0ml of 0.5M of freshly refluxed Na_2SeSO_4 was added and the volume was 50ml with water. The pH of the solution was adjusted by the use of 1.0ml, 3.0ml, 4.0ml, and 5.0ml of ammonia $NH_4(OH)$ in 8.9, 9.3, 9.7, & 10.0 baths, respectively. The degreased substrates were vertically suspended in the bath with a holder. After the 24hrs the substrate were taken out of the bath and rinsed with distilled

Reaction bath	Dip Time (hr)	Temp °C	pH	Average α (µm)	Average n	Average K	Average σ_{opt} (S^{-1})	Thickness, t (µm)	Bandgap, E_g (eV)	Average ε_r	Average ε_i
8.9	24	33	8.9	211863.0	1.954787	0.008139	1.0505E+13	0.050401	2.70	3.848349	0.032838

water, which after it was dried in air

RESULTS AND ANALYSIS

Table 1: Optical properties and thicknesses of NiSe films grown under varying pH.

9.3	24	33	9.3	72219.97	1.898311	0.007966	1.26946E+13	0.174229	2.60	3.705832	0.033693
9.7	24	33	9.7	239583.3	1.913801	0.009132	1.59867E+13	0.237931	2.50	3.80445	0.040622
10.0	24	33	10.0	495702.5	2.035661	0.015499	2.66477E+13	0.512032	2.45	4.300316	0.068787

Table 2. The variations in the pH, volume of the $NH_4(OH)$ and thickness

Reaction bath	pH	Vol.of $NH_4(OH)$ Solution (ml)	Thickness (μm)	Bandgap(eV)
8.9	8.9	1	0.050401	2.70
9.3	9.3	3	0.174229	2.60
9.7	9.7	4	0.237931	2.50
10.0	10.0	5	0.512032	2.45

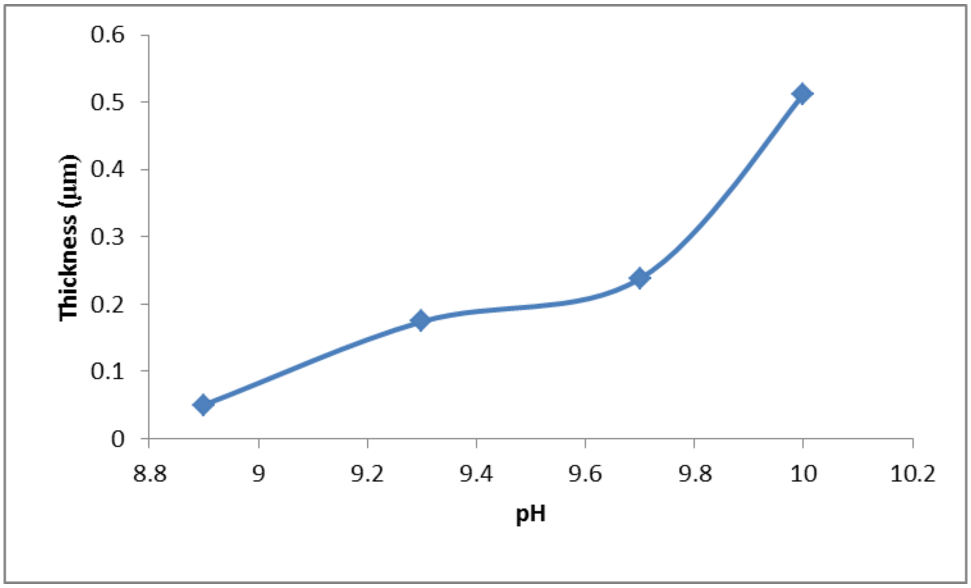

Fig. 1.0 Variation of thickness with pH of NH_4 (OH)

Optical Properties of Nickel Selenide (NiSe) Thin Films

Fig 1 shows that film thickness increases proportionally with increase in pH value of the reaction bath. This is likely due to the variation in the volume of the ammonium NH_4 (OH) solution used.

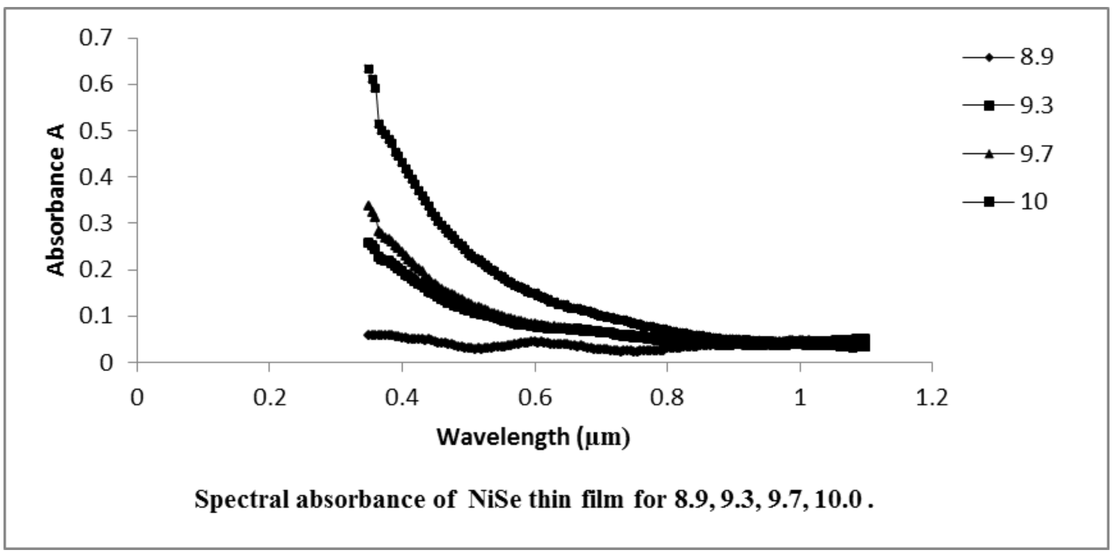

Fig. 2.0 Plot of Absorbance versus wavelength for pH of 8.9, 9.3, 9.7, 10.0 .

Fig 2 shows the variation of the optical absorbance spectra of the film with wavelength. Film prepared at 8.9 pH has low absorbance of (0.11- 0.115) at UV region of 350nm-400nm. At VIS-NIR-IR regions, it has (0.115-0.114). For films prepared at 9.3, 9.7, and 10.0 pH, the absorbance decreases proportionally with wavelength increase from UV-VIS-NIR-IR regions respectively.

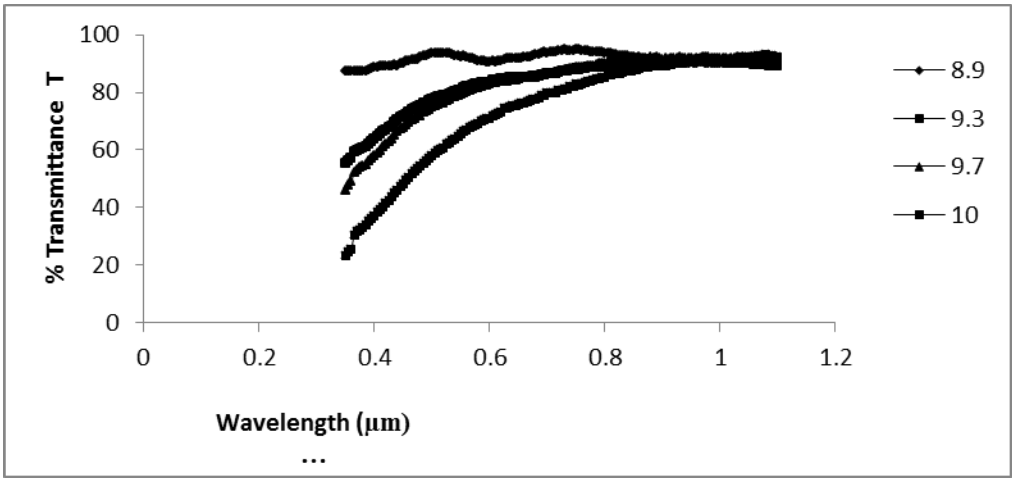

Fig 3.0 Plot of Transmittance versus wavelength for pH of 8.9, 9.3, 9.7, 10.0.

Fig.3 shows the variations of the transmittance spectra of the film with wavelength. The % transmittance for films prepared at 9.3, 9.7 and 10.0 pH, increases in all the regions between 70%-93% respectively. There was just a slight increase and decrease in all the regions for the film prepared at 8.9 pH. This could be as a result of low thickness of the film.

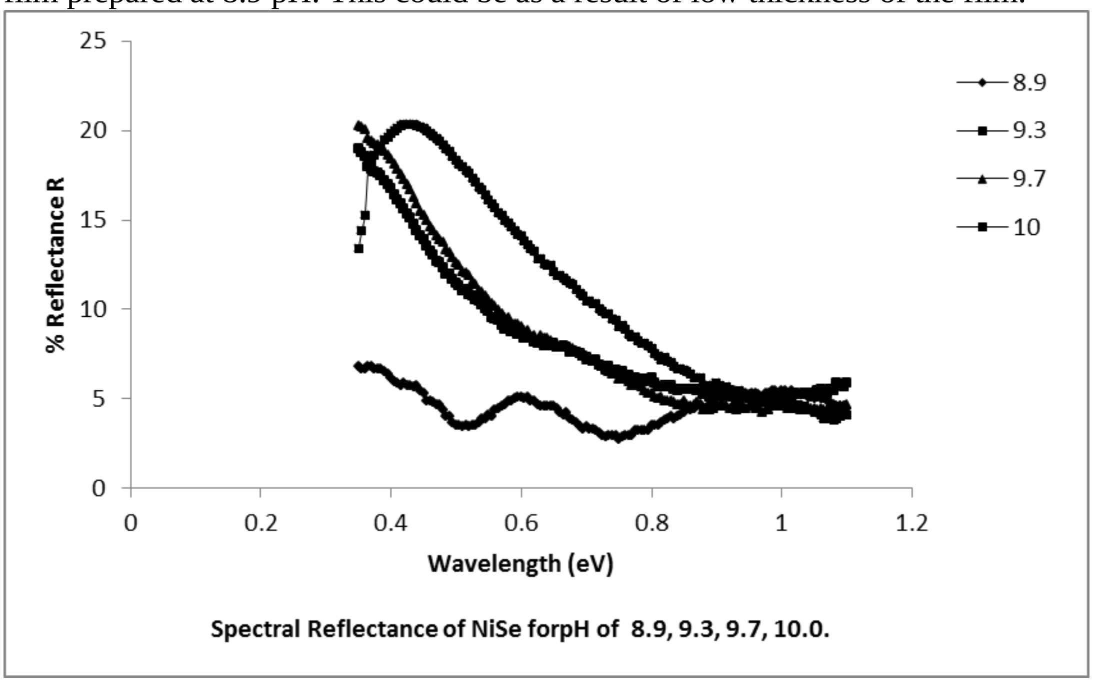

Fig 4.0 Plot of Reflectance versus wavelength for pH of 8.9, 9.3, 9.7, 10.0.

Fig 4 shows the variations of the reflectance spectra of the film with wavelength. Films prepared at 9.3, and 9.7 pH has % reflectance decrease in all the regions of values between18%-6.7%, but film prepared at 10.0 pH has an increase in the UV region of (350nm – 400nm) which ranges from 13.4% -21.0% . It then decreased from 21% to 4.1% at VIR-NIR-IR. Film prepared at 8.9 pH has a slight increase and decrease constantly throughout the regions which ranges from 8%-5% .

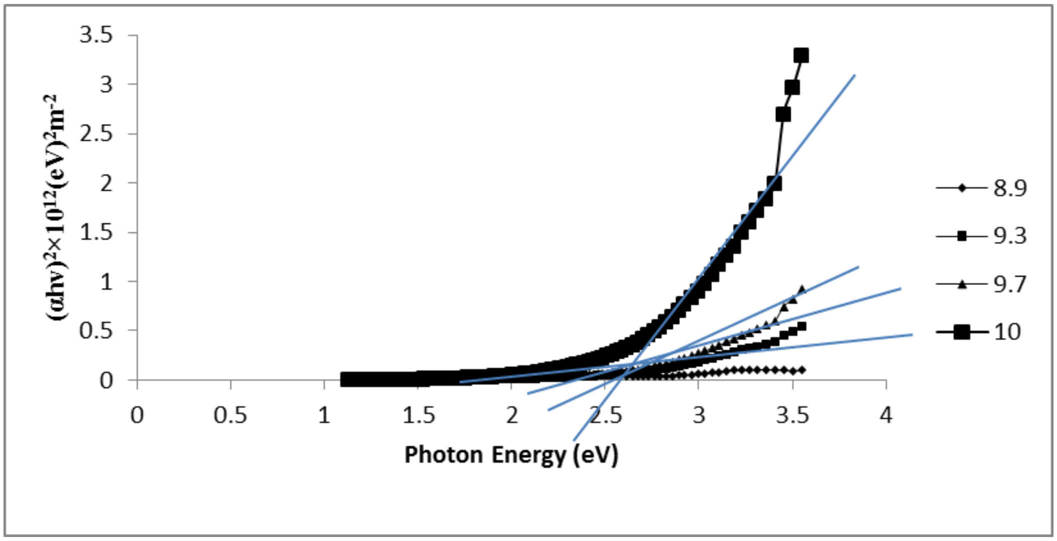

Fig 5.0 Plot of $(\alpha h\upsilon)^2$ versus photon energy of NiSe for pH of 8.9, 9.3, 9.7, and 10.00 .

Fig 5 shows the optical band gap (Eg) of the films estimated from $(\alpha h\nu)^2$ versus eV curve for prepared film at 8.9, 9.3, 9.7, and 10.0 pH, respectively. The straight nature of the plot indicates the existence of the photon energy axis at $(\alpha h\nu)^2 = 0$. The band gap energy decreases with increase in the pH of the reaction bath as was revealed in fig.6.0. The band gap energies were found to be 2.70eV, 2.60eV, 2.50eV, and 2.450eV for pH values of 8.9, 9.3, 9.7, and 10.0 respectively. The band gap energy decreases as the pH value of the reaction bath increases as was depicted in figure 6.The decrease in bandgap was as result of increase in thickness. This result compares slightly with work of Anuar *et al.* (2011) who presented a band gap of 2.11- 2.52eV. The wide band gap possessed by NiSe film makes it likely candidate to replace GaN in light emitting laser diodes (Prabahar *et al*, 2009). It is also a good material for window layer coatings.

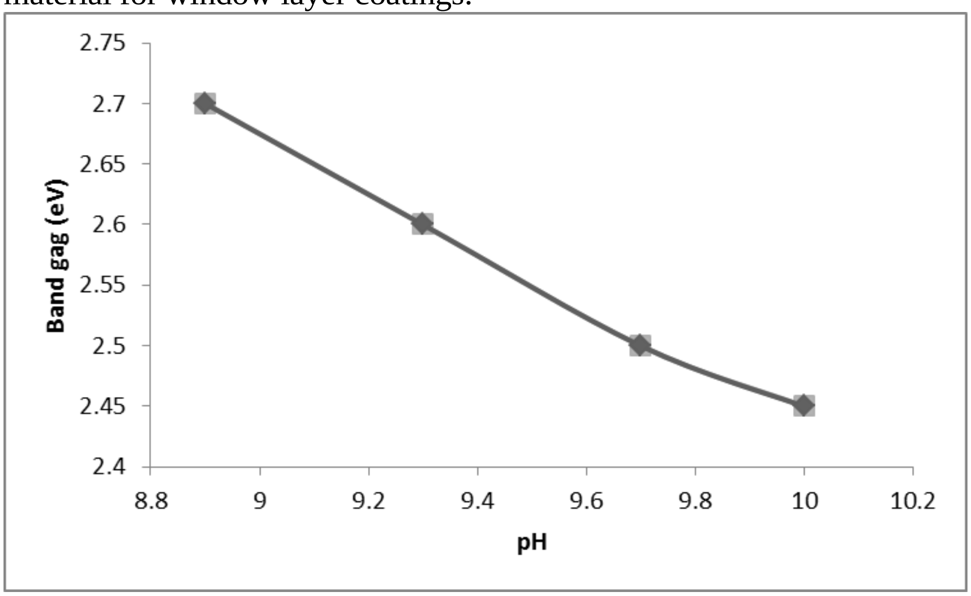

Fig.6.0: The variation of band bap with the pH of the reaction bath.

Fig6.0 shows that the band gap increases as pH increases

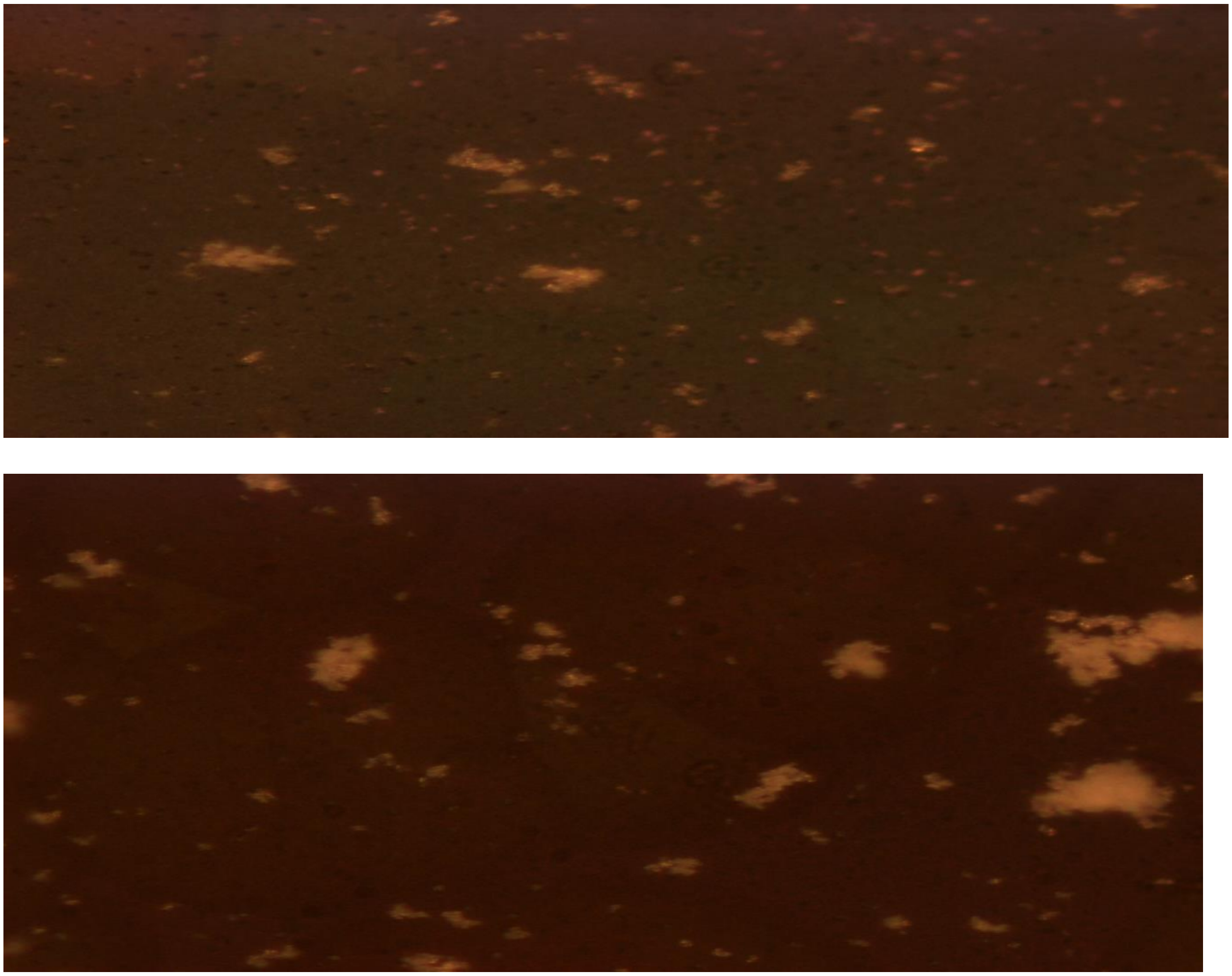

Fig 6.0 Photomicrograph of NiSe thin films for pH of 9.7 at 100 x

The surface morphology of sample was investigated using scanning electron microscopy (SEM). Figure 6 shows the SEM micrograph of NiSe thin film deposited on the microscope glass slide at 200x magnification. The thin film is composed of largely irregular-shaped grains of diameter 1-10 μm. This is due to several crystallites grouped together to form larger grains.

Summary

We have successfully deposited Nickel Selenide (NiSe) thin film using cheap and simple solution growth technique, and characterized the deposited films using the optical microscope and spectrophotometer to obtain the surface morphological and optical properties of the films.

The characterization of the films revealed the following:
NiSe have band gaps (E_g) of 2.45eV – 2.70eV, thicknesses ranging from 0.05μm – 0.51μm.
Due to the high absorbance and low reflectance in the ultraviolet, visible and infrared regions, NiSe thin films are suitable for coatings on different types of solar collectors.

5.2 CONCLUSION

In conclusion therefore, NiSe thin films have been obtained by chemical bath deposition method in the presence of disodium ethylenediaminetetraacetate. The NiSe thin films deposited at higher pH value showed higher absorbance value. The energy band gaps obtained were found to be 2.45 – 2.70eV.

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