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Exciton Contribution to the Photoemission from Thin Films of Solid Argon[+++]

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The photoelectric yield and the reflectance of solid Ar films on an Au substrate have been measured simultaneously for photon energies 10-30 eV. The thickness ranged from 30-300 Å. The synchrotron radiation of DESY was used as a light source. Even for photon energies below the photoelectric threshold of solid Ar there is some photoemission due to contributions from both the Ar film and the gold substrate. The spectra of the yield per absorbed photon exhibit peaks at the exciton energies. The height of the peaks is almost independent of the film thickness. This indicates that exciton decay at the Ar-vacuum or Ar-Au boundary contributes to photoemission.

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1. Introduction

The current search for efficient laser mechanisms in the vacuum ultraviolet has increased the interest in the electronic structure of solid rare gases[1]. The optical properties have been studied extensively by absorption[2] and reflection[3] spectroscopy. Radiationless electronic energy transfer phenomena have been investigated by studying the vacuum ultraviolet emission from gaseous, liquid and solid rare gases and rare gas mixtures[4].

Comparatively little is known about photoemission of electrons from solid rare gases, a process which becomes competitive to light emission as a decay channel. So far only yield measurements have been performed by O'Brien and Teegarden[5] for solid Kr and Xe for photon energies below the LiF cut off and by three of the present authors[6] for photon energies between 10 and 32 eV for Ar, Kr and Xe. In these investigations a comparatively low yield was observed in the excitonic range of the spectrum. For photon energies in excess of E_G+E_A (E_G gap energy, E_A electron affinity) strong photoemission sets in due to interband transitions. Since at least the first exciton states lie below the vacuum level a decay of these excitons via ionisation of defects or impurities was assumed in order to account for their contribution to photoemission. Indeed recent photoemission experiments on rare gas mixtures, where guest atoms or molecules of known concentration serve as such impurity states have corroborated this hypothesis[7]. In these experiments a strong increase of the photoemission yield in the exciton range due to doping is observed. Alternatively one may think of a decay of the excited states at the surfaces (the rare gas-vacuum or rare gas-substrate boundary). The aim of the present investigation was to study these effects in more detail.

2. Experimental Procedure

The yield measurements on solid Argon were performed with synchrotron radiation of the Deutsches Elektronensynchrotron DESY as a light source[8] . At the exit arm of a near normal incidence monochromator in a modified Wadsworth mount[9] an ultra high vacuum chamber was attached. The pressure was in the low 10^{-10} Torr range. The Ar films where prepared by evaporation on to a cooled gold coated quartz crystal. A liquid He flow cryostat with two shields was used to cool the substrate. By rotation around an excentric pivot the sample could be moved out of the light path for the measurement of the incident photon flux with an open electrostatic photomultiplier. During the yield measurements this multiplier served in the reflection position as a detector for a simultaneous recording of the reflectance. An electric field of 2000 V/cm at the collector grid was chosen in order to insure saturation of the photocurrent. For the determination of the absolute photoyield per incident photon, the absolute intensity of the incoming photonflux was determined with a Samson double ionization chamber[10] placed at the exit slit of the monochromator. Under typical working conditions of the synchrotron (4.5 GeV, 10 m A) a photon flux of 1 x 10^{+9} photons/Å sec was measured at 600 Å (20.66 eV). The absolute values for the yield thus obtained were furtner checked by comparing them to the measured photocurrent of the gold coated substrate before evaporation of the Ar films.

The purity of the Ar (supplied by L'Air Liquide) was better than 99.9997%. The base pressure in the ultrahigh vacuum gas handling system was also in the 10^{-10} Torr range before it was filled with 1000 Torr of Ar. The gas flow and therefore the rate of growth of the films, typically 1 Å/sec, was controlled by means of a needle valve. The temperature of the substrate was around 12 K. The growth of the films was monitored during deposition of the gas by measuring continuously the reflectance at 1200 Å where strong inter-

ference effects are observed. For the calculation of the film thickness the formulae of Ref. 11 were applied to the Ar-Au-sandwich. We used the optical constants for gold from the literature[12] . Values for n and k for Ar were obtained by a Kramers-Kronig analysis of reflectance data for a thick Ar-film, where no interference effects are present.

3. Results and Discussion

In Fig. 1 the results of the yield measurements in the excitonic part of the spectrum are shown for five different film thicknesses. In the measured spectra of thin films (d_1,d_2; left side) peaks occur at the exciton energies. For the thicker films the yield spectra exhibit dips at positions of the first spin orbit split exciton bands. There is a comparatively high yield of approximately 10% for the Ar-Au-system even for those energies where the Ar films are transparent. This is explainable by the fact, that light penetrating through the Ar film may excite photoelectrons in the gold substrate. These electrons escape through the Ar film into the vacuum and contribute to the total photoyield. For this process a high penetration length of free electrons in solid Ar has to be assumed[6] . This is not inconsistent with results obtained for liquid Ar[13] .The dip occuring in the yield curves at the exciton frequencies for the thicker films is mainly due to the larger reflectance within the exciton bands. Less light reaches the gold substrate and hence the contribution from Au to the total yield is reduced.

In order to get a more quantitative estimate for the yield from the pure Ar the measured total yield curves (Y_m) were corrected for the reflectance from the vacuum-Ar interface and for the contribution from the gold substrate (Y_{Au}) as well as for second order light from the monochromator (Y_2) ($\simeq$ 3% at 11 eV). The last two corrections are entirely structureless. Hence, the corrected yield

Y_c normalized to the photon flux penetrating into the Ar film (shown on the right hand side of Fig.1) is given by

$$Y_c = \frac{Y_m - Y_2}{1 - R} - Y_{Au}$$

where R is the reflectance (Fig.2) measured simultaneously together with the yield for each film thickness. The first term on the right hand side of the expression for the yield Y_c represents the yield per absorbed photon. The subtraction of the gold yield from the total yield as described above, assumes that all electrons, once they have escaped from the gold into the Ar, can penetrate the Ar film and are collected. The analysis of our data shows that this assumption is reasonable for the range of thicknesses shown in Fig.1. Because we neglect the absorption of light within the Ar film, we obtain only a lower limit for the Ar yield per absorbed photon. Dividing the measured curves (Fig.1, left side) by 1-R we obtain an upper limit well below 20%. The main contribution to the change of the structure going from the left part to the right part of Fig.1 comes from the normalization factor 1/(1-R). Obviously, the change of the reflectance with film thickness(Fig.2) accounts for most of the changes of the yield curves with increasing film thickness.

However, apart from the details of the yield curves, the important observation is that the yield Y_c does not change markedly with film thickness in the excitonic part of the spectrum. This is in contrast to the yield behavior above the sharp onset of photoemission, as is apparent from the spectra shown in Fig.3. Here the yield spectra are shown for the entire range of 3p valence electron excitation. For energies above threshold the yield rises strongly with increasing filmthickness, reaching values of up to 0.7 for films 300 Å thick. This different dependence of the yield on film thickness for excitation energies below and above threshold is shown for two photon energies in Fig. 4.

One of the possible decay processes of excitons leading to photoemission, namely ionization of defect or impurity states, would depend on film thickness, because the number of such sites would increase with thickness. This holds provided the range of exciton

migration or energy transfer is large enough. This is supported by a strong increase of the yield with film thickness in the excitonic range of the spectrum for Ar films doped with Xe[7]. One is thus led to the conclusion that in the investigated undoped Ar films the decay via ionisation of impurities or defects is not the dominant mechanism for photoemission in the excitonic range. This indicates that exciton decay at the vacuum Ar or the Ar-Au boundary contributes to photoemission.

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Figure 1 : Yield for photoemission in the excitonic range of the spectrum at 12 K for five films of Ar on Au with different thickness d_1 = 30 Å, d_2 = 75 Å, d_3 = 140 Å, d_4 = 225 Å and d_5 = 300 Å. The left part gives the measured yield per incident photon, the dashed curves indicate the gold yield without Ar. The right part gives the corrected yield, (see text).

Figure 2 : Reflectance for thin Ar films on Au substrate at 12 K. d_1 to d_5 are the same as in Fig.1. Note that even for d_6 = 1400 Å interference effects from the gold substrate are present, e.g. maximum at 13.24 eV.

Figure 3 : Photoyield for Ar on Au at 12 K for five different film thicknesses d_1 to d_5 (see Fig. 1). The dashed curve is the reflectivity for d_5 as in Fig. 2

Figure 4 : Dependence of the photoyield with corrections as discussed in the text on the thickness of the Ar-film for $\hbar\omega$ = 12.25 eV (excitonic part of the spectrum) and $\hbar\omega$ = 18 eV (above threshold).

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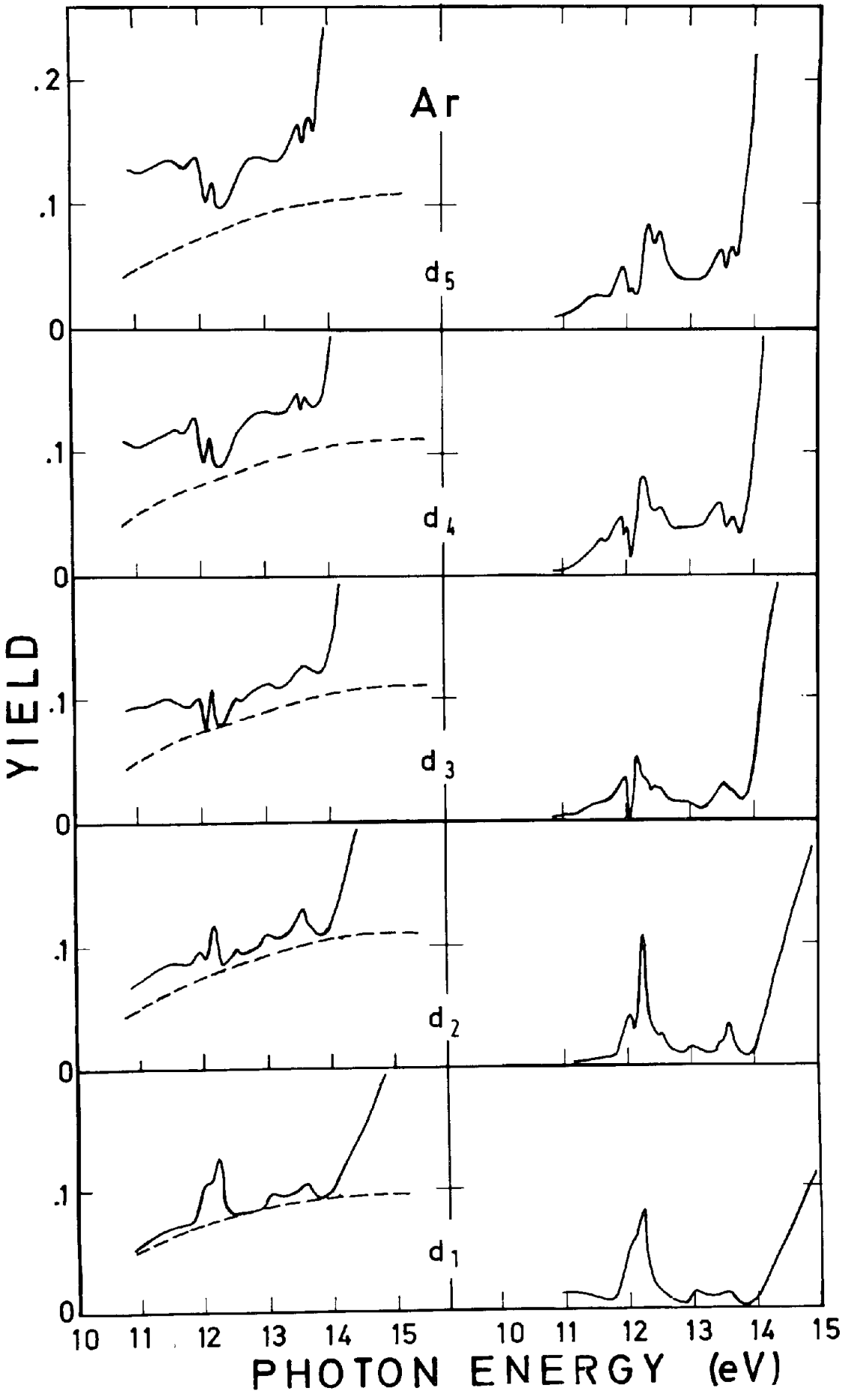

Fig.1

ARGON
REFLECTANCE
PHOTON ENERGY (eV)
d1
d2
d3
d4
d5
d6
12.07
12.25
12.65
13.15
13.65
13.87
12.05
12.22
12.80
13.12
13.57
13.80
11.88
12.05
12.27
12.45
12.55
13.50
13.72
14.05
11.75
12.05
12.30
12.50
12.60
13.35
13.57
13.70
14.05
11.95
12.10
12.35
12.54
12.65
13.25
13.63
13.77
13.93
14.10
11.70
12.07
12.25
12.53
12.82
13.24
13.59
13.76
13.90
14.04
14.12

Fig. 2

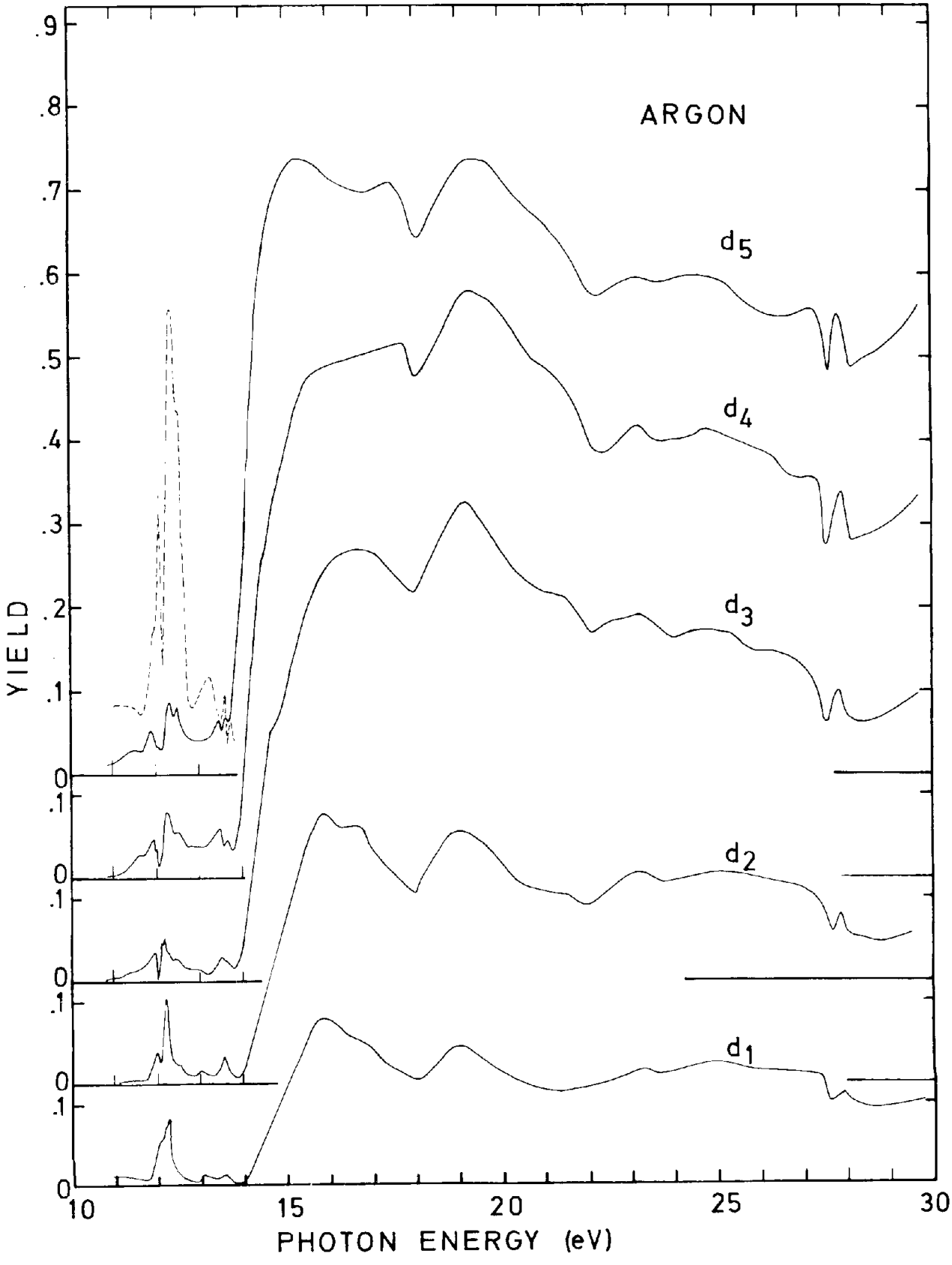
ARGON
d5
d4
d3
d2
d1
YIELD
PHOTON ENERGY (eV)
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
10
15
20
25
30

Fig.3

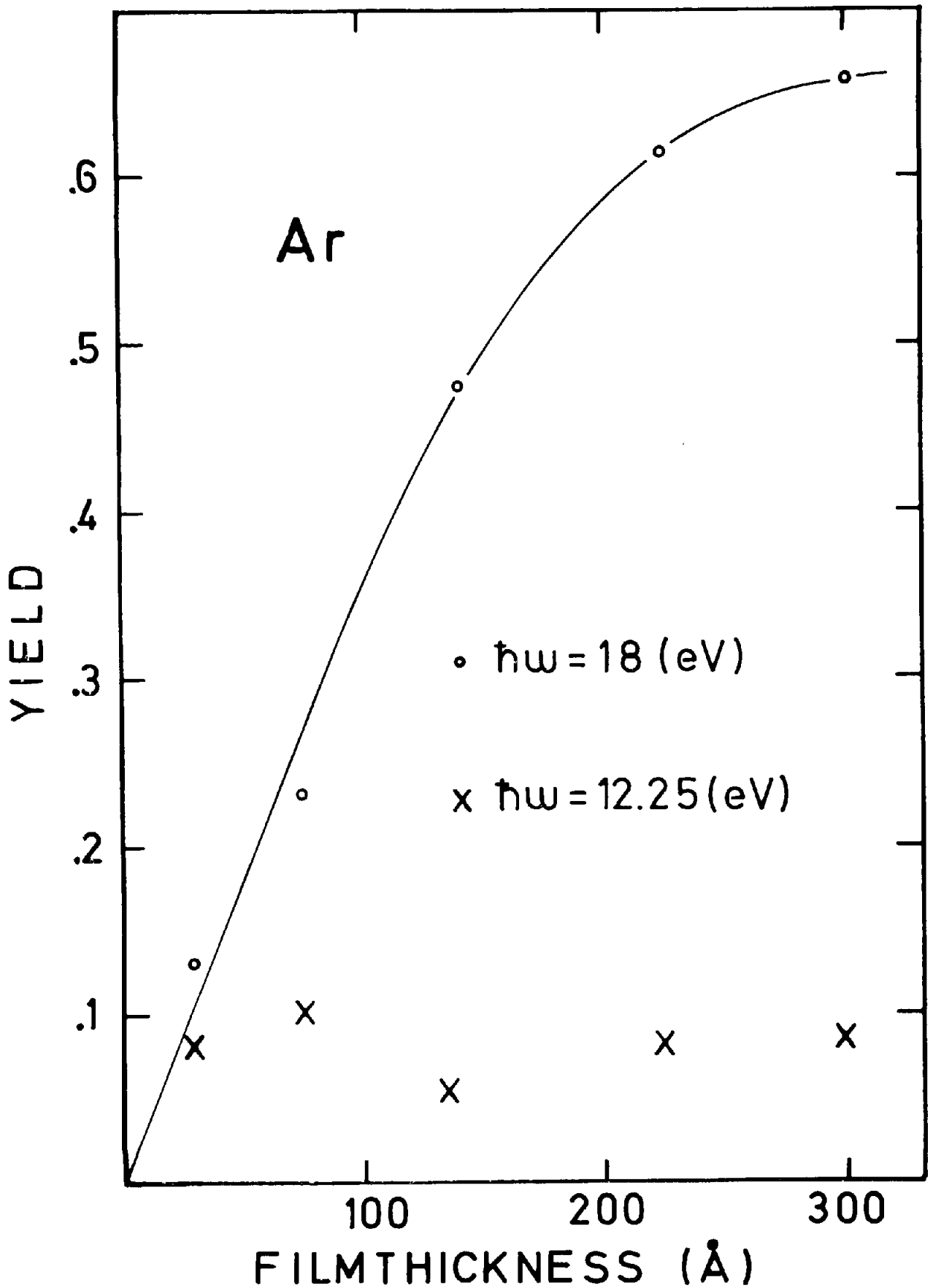
Ar
YIELD
.6
.5
.4
.3
.2
.1
ħω = 18 (eV)
x ħω = 12.25 (eV)
100
200
300
FILMTHICKNESS (Å)

Fig.4