OLVASÓTERMI PÉLDÁNY
TK 155.132

KFKI-1980-05

G. PETŐ
J. KANSKI

PHOTOEMISSION SPECTRA OF ION-IMPLANTED AMORPHOUS Si AND $Fe_{84}B_{16}$ METAL-GLASS

Hungarian Academy of Sciences

CENTRAL RESEARCH INSTITUTE FOR PHYSICS

BUDAPEST

2017

KFKI-1980-05

PHOTOEMISSION SPECTRA OF ION-IMPLANTED AMORPHOUS Si AND $Fe_{84}B_{16}$ METAL-GLASS

G. Pető J. Kanski*
Central Research Institute for Physics
H-1525 Budapest 114, P.O.B.49. Hungary

*Department of Physics, Chalmers University of Technology, Gothenburg, Sweden. S41296

HU ISSN 0368 5330
ISBN 963 371 628 4

ABSTRACT

Ultraviolet photoemission spectra /U.P.S/ of Si and $Fe_{84}B_{16}$ were measured in amorphous and crystalline state at 10,2 eV exciting photon energy. The surface composition were determined simultaneously by the A.E.S method. The samples were prepared by ion-implantation, evaporation or by splat-cooling. The photoelectric spectra of amorphous phases are different from the crystalline for all materials and preparation methods. The U.P.S of amorphous silicon and $Fe_{84}B_{16}$ metal-glass have some common and some different characteristics.

АННОТАЦИЯ

Изучалась фотоэмиссия аморфных и кристаллических фаз Si и $Fe_{84}B_{16}$ при возбуждении фотонами с энергией 10,2 эВ. Параллельно с этим исследовался состав поверхностного слоя методом АЭС. Образцы изготовлялись ионным внедрением, вакуумным испарением и методом быстрого охлаждения разплава. Для обоих материалов и при любом из перечисленных методов изготовления образцов фотоэмиссия кристаллической и аморфной фаз значительный отличалась друг от друга. Спектры фотоэмиссии аморфным Si и $Fe_{84}B_{16}$ имели одновременно схожие и отличные друг от друга свойства.

KIVONAT

Si és $Fe_{84}B_{16}$ fotoemisszióját vizsgáltuk amorf és kristályos állapotban, 10,2 eV-os gerjesztő foton energiával. A felületi összetételt A.E.S módszerrel vizsgáltuk, ezzel párhuzamosan. A mintákat ionimplantációval, párologtatással és gyors-kötéssel készitettük. A kristályos és amorf fázis fotóemissziója lényegesen különbözött egymástól, mindkét anyag és mindegyik mintakészités esetén. Az amorf Si és $Fe_{84}B_{16}$ fotóemissziós spektruma azonos és eltérő tulajdonságokat egyaránt mutat.

The density of states in topologically random systems has been investigated theoretically and experimentally, several density of states calculations and experiments have been carried out for tetrahedrally bonded semiconductors /1-8/.

The experimental work demonstrated that the band structure of amorphous Si is different in some way from the crystalline.

The differences are concentrated mainly at the lower lying s-level, the p states are mainly unchanged. The tailing effect at the valence band edge has not been detected by the U.P.S method /3,4,5/. Moreover it is suggested that the tailing effect of the valence band is not a feature of carefully prepared amorphous semiconductors /6/.

Far less attention has been directed at these problems in amorphous metals. Theoretical calculations show that in amorphous metals the electronic spectrum is broadened whereas the gross features are unchanged /10,11/. The experimental results show some change in electronic structure mainly near the Fermi level in other alloys /12,13/. It is accepted that the electron structure of amorphous materials dependent on the preparation technique and crystalline states. An interesting question might be as to the general features of the electron structure on amorphous materials which are independent of the crystalline form and preparation method.

The main goal of our experiments is to study the electron structure of condensed materials. For this purpose different electronic systems such as metal-glass /FeB/ and amorphous semiconductor /Si/ were chosen, the samples were prepared by widely different methods /ion-implantation, evaporation, splat-cooling/. For reference purpose and for checking the experiments, the samples were crystallized in-situ.

The a-Si was prepared by ion-implantation /40 keV Si^+ with

1000 μC dose/ on the <111> surface and evaporation /at 10^{-4} Pa , with 0,2-0,3 nm/s evaporation speed/ on a Si<111> substrate at room temperature. The splat cooling at room temperature was used to prepare iron boron metal-glass with the composition Fe 84 at% B 16 at%. The crystalline phase was realized by heat-treatment /550°C 1 hour at 10^{-5} Pa/ and by removing the ion-implanted layer /0.1-0.2 μm/ with 3 keV Ar^{+} ion bombardment for a-Si and annealing /630°C 1 hour at 10^{-5}Pa/ for Fe-B metal-glass. After the annealing the sample surfaces were cleaned again.

The samples were cleaned by Ar^{+} ion bombardment with 0.8-1 keV energy, 30-50 $\mu A/cm^{2}$ current-density. The photoelectron spectrum /U.P.S/ was simultaneously examined with surface composition measurement /A.E.S/. The energy of photoelectrons was analysed by a retarding field method with ± 0.15 eV resolution, an exciting photon energy of 10,2 eV and 10^{-8}Pa pressure were used for the experiments. The E.D.C:s are given in arbitrary units as a function of the photoelectron energy. The A.E.S measurements were performed by PH.J 10-155 type CMA with the following parameters: exciting electron energy 2 keV, current 3 μA and the V_{pp} = 2 Volt.

The comparison of amorphous with crystalline states in the Si case is simple as the crystallized specimen will be single or policrystalline Si. The iron-boron system with this composition in the crystalline state consists of two phase but the U.P.S spectra of this system should be more or less similar to the α-Fe.

Independent methods /T.E.M, $^{4}He^{+}$ Rutherford back-scattering, χ-ray diffraction/ were cited to check the amorphous samples.

The E.D.C /a,b/ and A.E.S /c/ curves for ion-implanted a-Si are given in Fig.1. The high energy part of the E.D.C:s · 2,5 /b/ is given as an insert to the figure.

As shown, on the curve /c/ the sample has C, O contaminations on the surface at 2-3 at% concentrations though these contaminations do not disturb the photoemission spectra. The E.D.C:s /a,b/ have a very large secondary peak /S.P/ with a smooth and structureless part for the high energy photoelectrons,

there is only one break point /A/. This point /A/ divides the secondary peak from the valence band emission /V.B.E/ part. The V.B.E part of E.D.C:s has no edge. The small ratio /0.1/ of photoelectrons at 5 eV energy to the 2 eV energy is remarkable. Figure 2. shows the E.D.C /a/ and A.E.S curve for evaparated a-Si. The A.E.S data are the same as in Fig.1. The E.D.C:s is similar to the ion-implanted sample but the S.P is smaller and the V.B.E is larger and has a structure. The ratio of V.B.E at 5 eV to S.P is larger than for the ion-implanted sample /0.18/. The spectrum has no sharp edge, but the tailing effect is not so pronounced. The E.D.C and A.E.S curves for crystalline silicon are in Fig.3. The /a/ curve gives the <111> surface case when the ion-implanted layer had earlier been removed by ion bombardment and the /b/ curve represents the ion-implanted sample after annealing. Curve /c/ shows the A.E.S spectra for these surfaces. The units on the E.D.C axis are 2,5 times smaller than on Fig.1. and Fig.2. It is seen that the surface contaminations are the same for both the amorphous and the crystallized sample. After crystallization the spectrum of the E.D.C:s is markedly different from the amorphous one. The data in Fig.3. are in agreement with other results for crystalline silicon. The secondary peak considerably decreased, the V.B.E increased and has a definite structure. There is a sharp edge. The ratio of V.B.E at 5 eV to S.P. is 0.5, times larger than in the amorphous case. As the curve /b/ shows, the crystallization process was not completed by this heat-treatment because now the E.D.C:s not equal to the sputtered one. The differences are due to the amorphous characteristics. The ratio of photoelectrons at 5 eV to the 1,5 eV energy, is 0.4.

Figure 4 shows the FeB system. Curve /a/ gives the U.P.S and curve /c/ the A.E.S results. The details of the high energy part of the E.D.C:s are given by 2 times magnification /b/, the composition of the surface is $Fe_{84}B_{16}$ similarly to the bulk and the contamination is 5-6% C and 6-8% O.

The E.D.C:s /a,c/ have a large secondary peak, a smooth and structureless part at the high energy range with Fermi edge.

A definite break point /A/ separates the high energy range from the secondary peak, the ratio of photoelectrons at 5 eV to 1.5 eV energy is 0.3.

Figure 5 represents the U.P.S and A.E.S curves after crystallization. The units on the E.D.C axis are 2.5 times smaller than on Fig.4. The A.E.S curve shows that the surface contamination did not change compared with amorphous sample and the photoemission spectrum should be changed only by the crystallization process. The E.D.C:s is characterized by a structureshaped band emission range and a lower secondary peak. The ratio of the emission range at 5 eV energy to the secondary peak is 0.5 larger than in the amorphous case.

It is clear from Fig. 1-5 that the E.D.C:s of a-Si and FeB metal-glass are considerably different from the crystalline one. There are some similar pecularities as the high energy part of the E.D.C:s has no structure and the inelastic part /S.P/ is remarkably enlarged. A sharp breakpoint separates the secondary peak from the band emission range of the E.D.C:s. The disappearance of the valence band edge in a-Si and the definite Fermi edge in FeB metal-glass illustrate the differences between the E.D.C:s of a-Si and those of FeB metal-glass.

The explanation for the structureless characteristics of the high energy part of the E.D.C:s is the broadening of the 3 p states in silicon and of the d band near the Fermi level in FeB too. The reason for the large inelastic part /S.P/ is the broadening of the density of states above the Fermi level too as the scattered and secondary electrons have a higher excape probability when the empty density of states is broadened.

The lack of a sharp edge points to a strong tailing effect of the valence band for a-Si. The broadening of p states and the tailing of the valence band are in contrast to the other experimental rasults /2-6/. Only one paper indicates the possibility of some tailing effect /7/.

The possible reason is that the short range order which determines the band structure could be extremly changed by the ion-implantation. The surface cleaning process could not be the

source of this effect as the crystalline E.D.C:s was measured when the ion-implanted layer had already been removed by 3 keV energy Ar^{+}.

It is surprising that a similar E.D.C:s was obtained for hydrogenated a-Si with high hydrogen concentration at the valence band edge /9/.

The crystallized Si samples have the well-know properties of Si indicate the peak of the Si, 3p states and the sharp edge of the valence band. Crystallized FeB /αFe,Fe_2B/ has a d-like peak at the Fermi level similarly α-Fe as was supposed earlier. The secondary peaks of the crystallized samples are similar to those of the crystalline metals and semiconductors.

The broadening of the density of states below and above the Fermi level in FeB metal-glass is in agreement with the theoretical predictions for amorphous metal and these data are the first experimental indications.

Our results though limited suggest that the broadening effect of the density of states near the Fermi level may be a general property of amorphous materials as it was experienced with very different kinds of electronstructures and preparation methods.

References

1. J.D. Joannopaulos, M.L. Cohen.
Solid State Physics. 31. 1976

2. L.Ley, S. Kowalczyk, R. Pollak, D.A. Shirley
Phys.Rev.Lett. 29. 1088 /1972/

3. T.M. Donovan, W.E. Spicer
Phys.Rev.Lett. 21. 1572 /1978/

4. T.M. Donovan, W.E. Spicer, J.M. Bennett, E.J..Ashley
Phys.Rev. B.2. 397 /1970/

5. D.T. Pierce, W.E. Spicer
Phys.Rev. B.5. 3017 /1972/

6. J.E. Fischer, T.M. Donovan, W.E. Spicer
Comments on Solid State Phys. /1973/

7. T.E. Fischer, M. Ebrudak
Phys.Rev.Lett. 27 /1971/

8. D.W. Bullett, M.J. Kelley
J. Noncryst Solids 32. 225 /1979/

9. B. von Roedern, L. Ley, M. Cardona
Phys.Rev.Lett. 39. 1576 /1977/

10. J.J. Rehr, R. Alben
Phys.Rev. B.16. 2400 /1977/

11. T. Fujiwara, M. Fuse, Y.Tanabe
J. Phys. Soc. Japan /Lett/. 44. 1397 /1978/

12. S.R. Nagel, J. Tanc
Phys.Rev.Lett. 35. 380 1975.

13. M.J. Kelley, D.W. Bullett
J. Phys. C. Solid State Phys. 12. 2531 /1979/

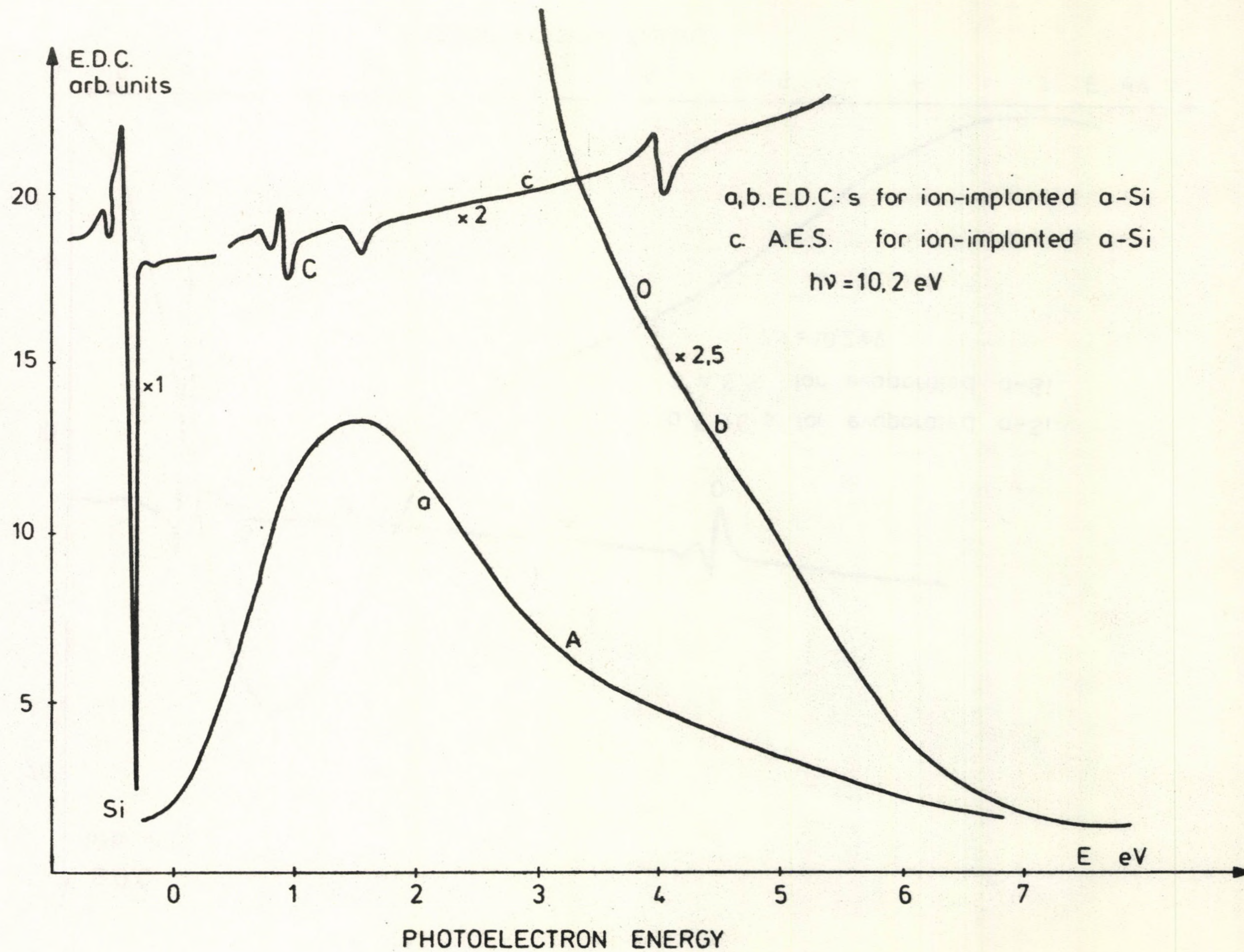

Fig. 1

U.P.S. and A.E.S. for ion-implanted a-Si

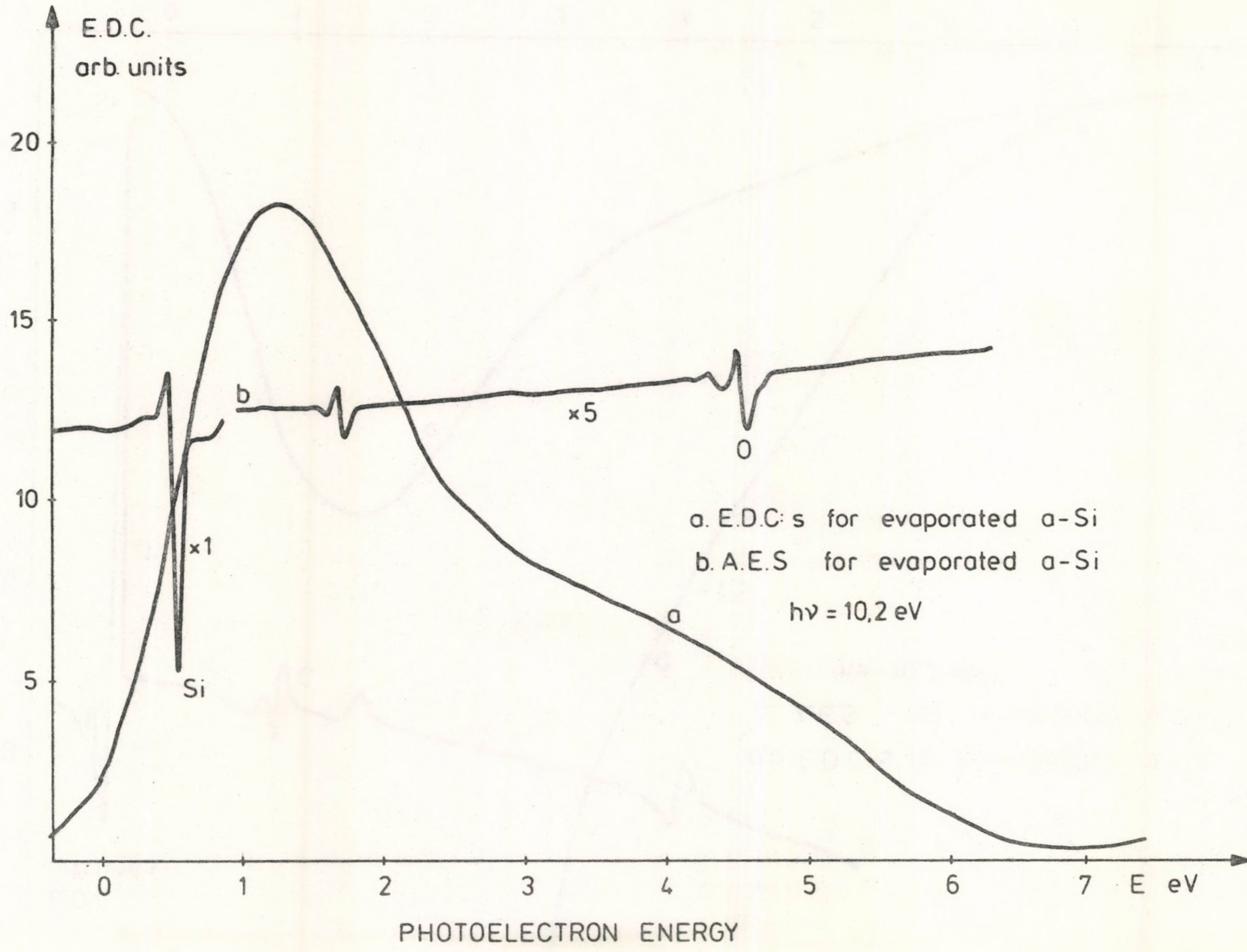

Fig. 2

U.P.S. and A.E.S. for evaporated a-Si

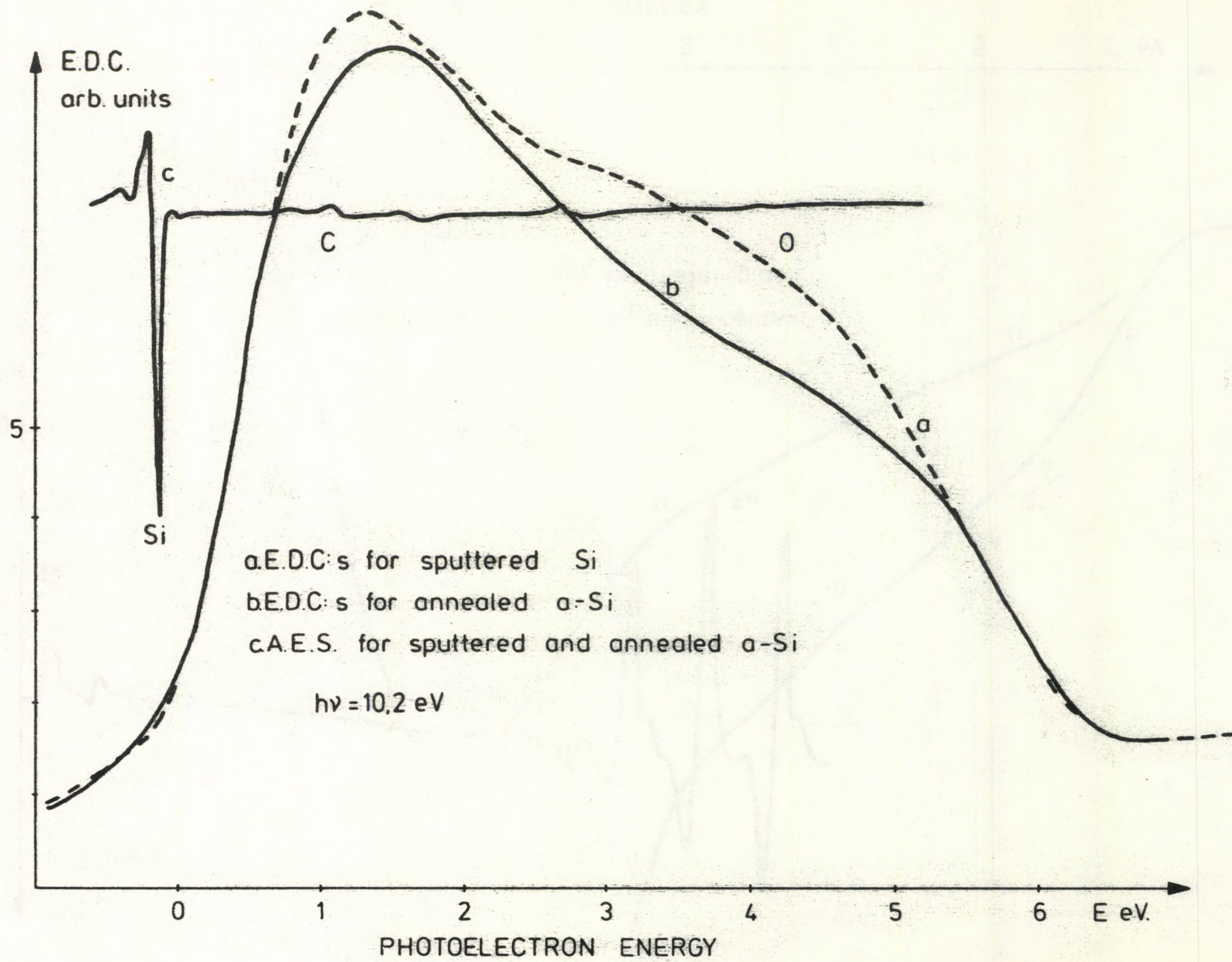

Fig.3

U.P.S. and A.E.S for in-situ crystallized Si

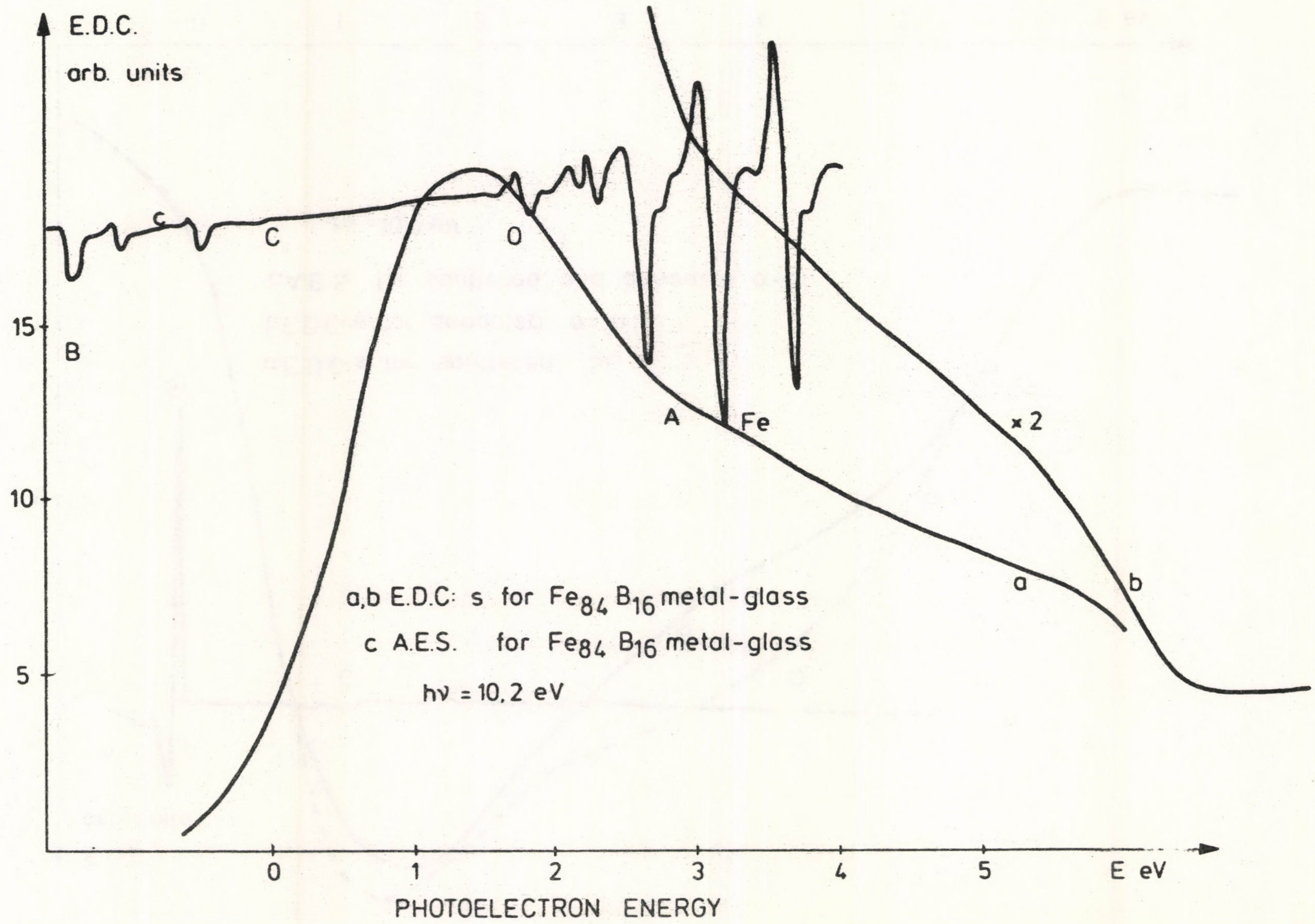

Fig. 4

U.P.S. and A.E.S for $Fe_{84}B_{16}$ metal-glass

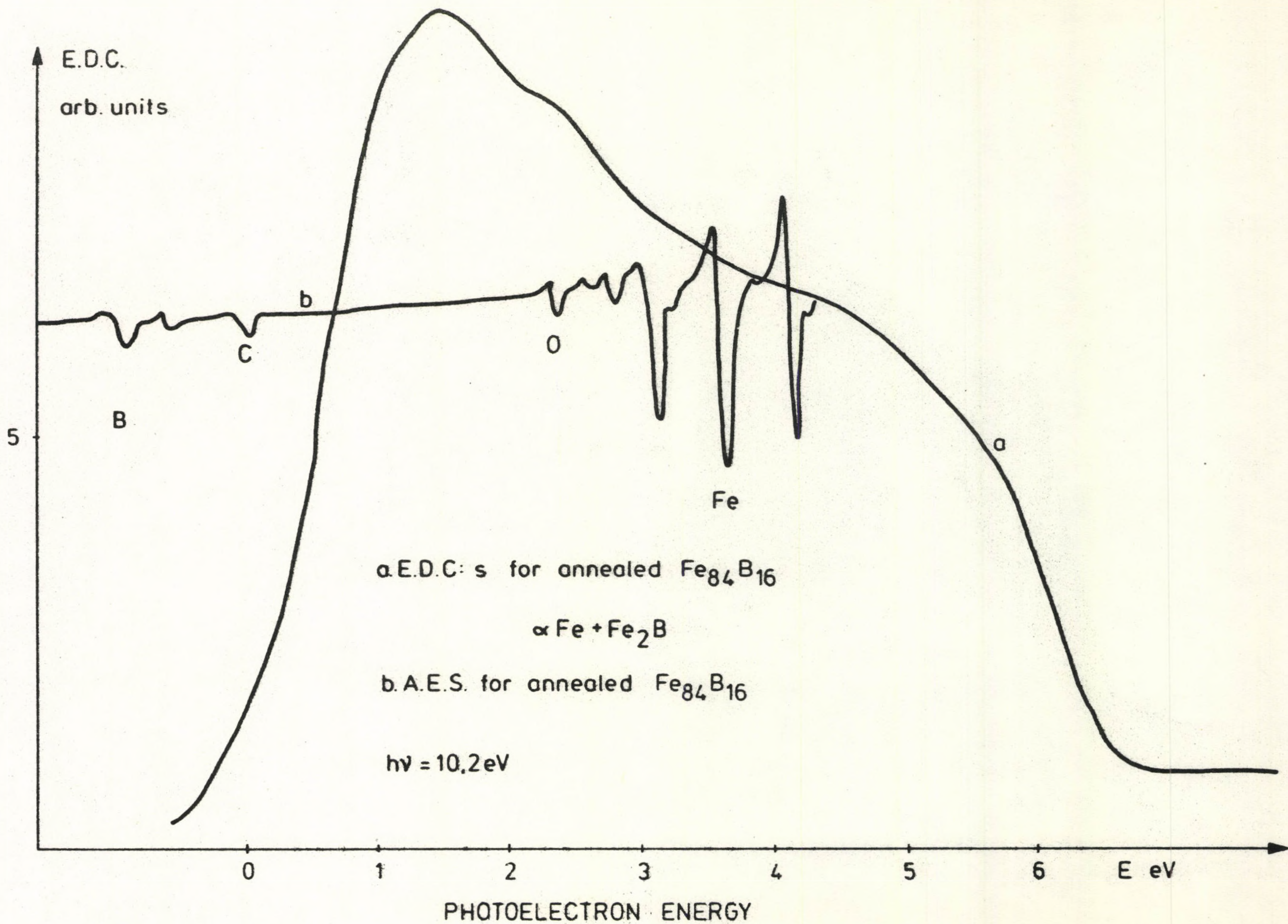

Fig. 5

U.P.S and A.E.S αFe, Fe_2B in-situ crystallized two phase system

62.986

Kiadja a Központi Fizikai Kutató Intézet
Felelős kiadó: Krén Emil
Szakmai lektor: Révész Péter
Jánossy András
Nyelvi lektor: Harvey Shenker
Példányszám: 255 Törzsszám: 80-32
Készült a KFKI sokszorosító üzemében
Budapest, 1980. január hó