Title

ENHANCED CRYSTALLINITY OF LOW TEMPERATURE DEPOSITED SILICON FILMS ON GRAPHITE SUBSTRATES

Author

Chang, Chin-An

Publication Date

1975-12-01

Submitted to Applied Physics Letters

LBL-3946 Rev.
Preprint c.1

ENHANCED CRYSTALLINITY OF LOW TEMPERATURE DEPOSITED SILICON FILMS ON GRAPHITE SUBSTRATES

Chin-An Chang and Wigbert J. Siekhaus

December 1975

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY

ENHANCED CRYSTALLINITY OF LOW TEMPERATURE DEPOSITED SILICON FILMS ON GRAPHITE SUBSTRATES

Chin-An Chang* and Wigbert J. Siekhaus

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
University of California, Berkeley, California 94720 **

ABSTRACT

Silicon thin films (2000-3000Å) were vacuum deposited onto graphite substrates held at 600°C with a prior coating of an ultrathin Si-Al-Si (~100Å-500Å-100Å) sandwich layer. X-ray diffraction showed a considerable increase in silicon crystallinity over those directly deposited onto graphites at the same substrate temperature. The increase observed is comparable to that using quartz substrates. The distribution of aluminum in the silicon films thus deposited is determined using Auger spectroscopic depth profiling.

---

*Present address: IBM, Thomas J. Watson Research Center,
Yorktown Heights, NY 10598

** Authors are also a part of the Energy and Environment Division.

Enhancement of thin film silicon crystallinity at low temperatures has been of interest for some time. Among the various studies are those which make use of the fact that silicon forms eutectic melts with several metals at rather low temperatures.[1,2] Using quartz substrate, the authors have shown one such technique to enhance silicon crystallinity for vacuum deposited silicon thin films.[1] Aluminum was chosen for this purpose which forms an eutectic melt with silicon at 577°C.[3] Ideally one would precoat the substrate at, say 600°C, with an ultrathin layer of aluminum on top of which the silicon film is deposited. However, aluminum is known to react with quartz[4] and is found to react with the ambient at 600°C in a vacuum of 10^{-6} Torr.[1] To overcome these difficulties, an ultrathin Si-Al-Si (100Å-500Å-100Å) sandwich layer was used to replace the single Al layer. This sandwich layer was deposited on quartz held at room temperature. The substrate was then heated to 600°C, at which temperature a thicker Si film (2000-3000Å) was deposited. Significant enhancement in silicon crystallinity was observed using this Si-Al-Si sandwich precoating technique. Transmission electron microscopic measurement showed a lower limit of 5μ for the average silicon grain size.[1] Optical microscopic measurement of the etched films further showed that silicon grains as large as 200μ were produced.[5]

In this work the same technique is applied to graphite substrates. Graphite is chosen because of its desirable properties as a substrate material for silicon thin film solar cells. Such properties include the electrical conductivity of graphite, its low cost and the low solubility of carbon in silicon at 1200°C.[6] The last property was deduced from data on the bulk systems. For the silicon thin films deposited on graphite our earlier work showed significant diffusion of silicon into graphite and carbon into silicon, and the formation of silicon carbide, at substrate temperatures above 1000°C.[7] At substrate temperatures below 800°C, however, such diffusion is greatly reduced.[5] Therefore, the above described Si-Al-Si sandwich coating technique should be applicable to the graphite substrate at 600°C to enhance silicon crystallinity without significant SiC formation. In addition, the difficulty encountered in our earlier study in determining the aluminum distribution is solved in the present work with an additional silicon over-coating as described later.

Silicon and aluminum were vacuum deposited onto graphite and quartz using conventional electron beam heating. The deposition rate was about 40Å/min for both Si and Al. An Allen Jones Electronic evaporation rate monitor was used in determining these rates and was precalibrated for both Si and Al. 99.9999% purity Si and Al were used for this work. The substrates used were commercial extruded graphite and fused quartz. Graphite substrates cut from a rod were used in both unpolished and polished form. The latter were polished on Grit 320 SiC paper. Both graphite and quartz substrates were used in each deposition, the latter being used as a reference for comparison with the earlier work.[1] The substrates were mounted onto a tantalum substrate holder which was heated by electron bombardment. Substrate temperatures were measured with a Chromel-Alumel thermocouple and an optical pyrometer. All substrates were cleaned with detergent and were ultrasonified before use. Prior to deposition, the substrates were outgassed at 800-900°C in a vacuum of 1×10^{-6} Torr. During deposition the vacuum remained in the 5×10^{-6} Torr region.

An ultrathin Si-Al-Si (100Å-500Å-100Å) sandwich layer was first deposited onto the substrates which were held at room temperature. The substrates were then heated to 600°C and a thin silicon film of about 2000-3000Å was deposited. Without further annealing the substrate heater was turned off and the substrates were allowed to cool down naturally. After the substrates reached room temperature, another layer of silicon (ca 300Å) was deposited. This last silicon coating serves to prevent oxidation of aluminum, most of which stays near the surface of the film.[1] It also helps to eliminate the presence of SiO_2 in the aluminum-rich region after exposing the film to air, since SiO_2 formation is restricted to a few monolayers. As is shown later, this overcoating allows a better Auger determination of the aluminum distribution in silicon films than that obtained previously.

It is recalled that in our earlier work, silicon grain sizes were directly determined using both transmission electron microscopy and optical microscopy. To apply the former technique the deposited silicon film was peeled off from quartz by immersing both into King's solution. The optical microscopic measurement was performed on the etched film without peeling off. Both techniques were found to be difficult to apply to the silicon films deposited on graphite. This was probably due to the rough and nonreflecting surface of graphite. Therefore, silicon crystallinity enhancement using graphite is inferred from the observed increase in silicon preferred orientation in the X-ray diffraction patterns. Silicon films from our earlier work showed highly preferred ⟨111⟩ orientation, with a (220)/(111) peak intensity ratio of 10-20%. When silicon was directly deposited onto quartz held at 600°C without the Si-Al-Si precoating, a (220)/(111) ratio of 60% was obtained. This is close to that of the silicon powder spectrum. Since the same Si-Al-Si precoating technique is used in both the earlier and present studies to enhance silicon crystallinity, the same mechanism of silicon crystallization from the Si-Al eutectic melt should be involved. Thus, by comparing the extent of increase in silicon preferred orientation an estimate of silicon crystallinity enhancement can be inferred. Figure 1 shows the X-ray diffraction patterns of the silicon films deposited on graphite and quartz. The latter is used as a reference to be compared with the earlier work. The (220)/(111) intensity ratios are ca 25% and 16% for the silicon films deposited on graphite and quartz, respectively. The enhancement in silicon preferred orientation using graphite is seen to be comparable to that using quartz. The latter, in turn, reproduces the 10-20% ratio of the earlier work.[1] Accordingly, the sizes of silicon grains produced using graphite are inferred to be of the order of microns. Furthermore, both polished and unpolished graphite substrates show the same enhancement in silicon crystallinity.

Also seen in Fig. 1b is a clear Al (111) peak which was not observed in the previous work using quartz substrate. This indicates the necessity of the described final silicon coating for the observation of aluminum. A similar but weaker Al (111) peak is also observed using graphite substrates. No attempt was made to compare the latter with a corresponding silicon film using graphite without the final silicon coating. The roughness of the graphite surface would probably make a meaningful comparison difficult. Figure 2 shows the Auger depth profiles of the same films. The Auger spectrometer used and the technique of obtaining depth profiles have been described elsewhere.[1,7] The 92 eV Auger line of silicon was used here. The silicon film deposited on quartz shows a higher concentration of aluminum near the surface than in the bulk film. This confirms our earlier observation that most aluminum was distributed close to the surface.[1] A similar but smoother aluminum distribution in the deposited silicon film is observed using graphite. Also noted is diffusion of both aluminum and silicon into the graphite substrate. Quantitative determination of the aluminum distribution in graphite is difficult due to the scattering of data and an uncertainty in the sputtering rate of graphite. Surface roughness of the graphite substrate could account for part of the diffuse interface observed. In the case of silicon film deposited on quartz, the Si Auger peak intensity reaches its maximum at a film depth corresponding to the 20-40 min sputtering region. Thereafter it continues to decrease with a shoulder at the 50-60 min sputtering region. From the known sputtering rate and film thickness, this shoulder region corresponds to the Si-SiO_2 interface. Normally, a clear Si-SiO_2

interface can be observed in the Auger depth profiling of a silicon film deposited directly on quartz.[5] The fact that in the present case no clear Si Auger peak of SiO_2 shows up after the interface has been reached is probably due to charging of the quartz surface. However, the main interest of showing Fig. 2b is the aluminum distribution profile in the silicon film which is not affected by the possible charging problem at the Si-SiO_2 interface. Our conclusion that most aluminum stays near the surface of the silicon film is, therefore, sustained.

The aluminum distributions described above are consistent with the observation that the aluminum (111) peak is more clearly seen in the silicon film on quartz than that on graphite. Carbon diffusion from the graphite substrate into the silicon film is much smaller than in the cases where graphite substrate temperature was above 1000°C. In several cases silicon deposition was made with a different Si-Al-Si sandwich coating. Using a Si-Al-Si (100Å-200Å-100Å) sandwich coating, the Si (220)/(111) intensity ratio was found to be similar to that using the Si-Al-Si (100Å-500Å-100Å) coating.

In summary, our work indicates that using graphite substrates, an enhancement in silicon crystallinity at low temperature can be obtained which is comparable to that using quartz substrates. Based on the latter work we presume that silicon grains with sizes of the order of microns are produced. Carbon diffusion into the silicon film can be significantly reduced using a substrate temperature of 600°C. Furthermore, graphite in the unpolished form gives an enhancement in silicon crystallinity similar to that on polished graphite. This may prove to be a further favorable economic factor in using graphite as a substrate material for silicon thin film solar cells.

ACKNOWLEDGEMENT

This work was done under the auspices of the U. S. Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the authors and not necessarily those of the Lawrence Berkeley Laboratory nor of the U. S. Energy Research and Development Administration.

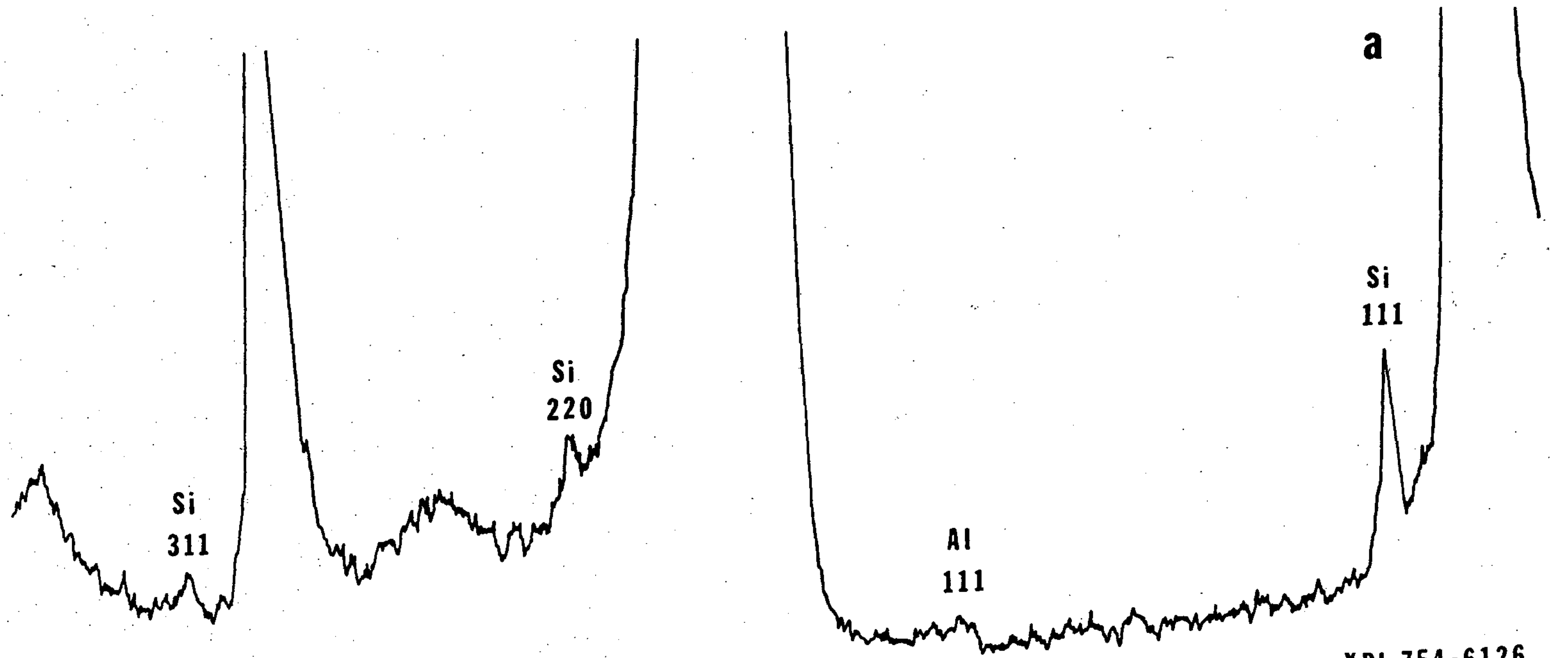
REFERENCES

1. C.-A. Chang, W. J. Siekhaus, T. Kaminska and D. T. Huo, Appl. Phys. Lett. 26, 178 (1975).
2. J. E. Davey, A. Christou and H. M. Day, Appl. Phys. Lett. 28, 365 (1976), and references therein.
3. R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gieser and K. K. Kelley, Selected Values of the Thermodynamic Properties of Binary Alloys (American Society of Metals, Cleveland, OH, 1973).
4. K. Prabiputaloong and M. R. Piggott, J. Electrochem. Soc. 121, 430 (1974).
5. C.-A. Chang, unpublished results.
6. R. I. Space and G. A. Slack, Proceedings of the Conference on Silicon Carbide (Pergamon Press, NY, 1960).
7. C.-A. Chang and W. J. Siekhaus, J. Appl. Phys. 46, 3402 (1975).

FIGURE CAPTIONS

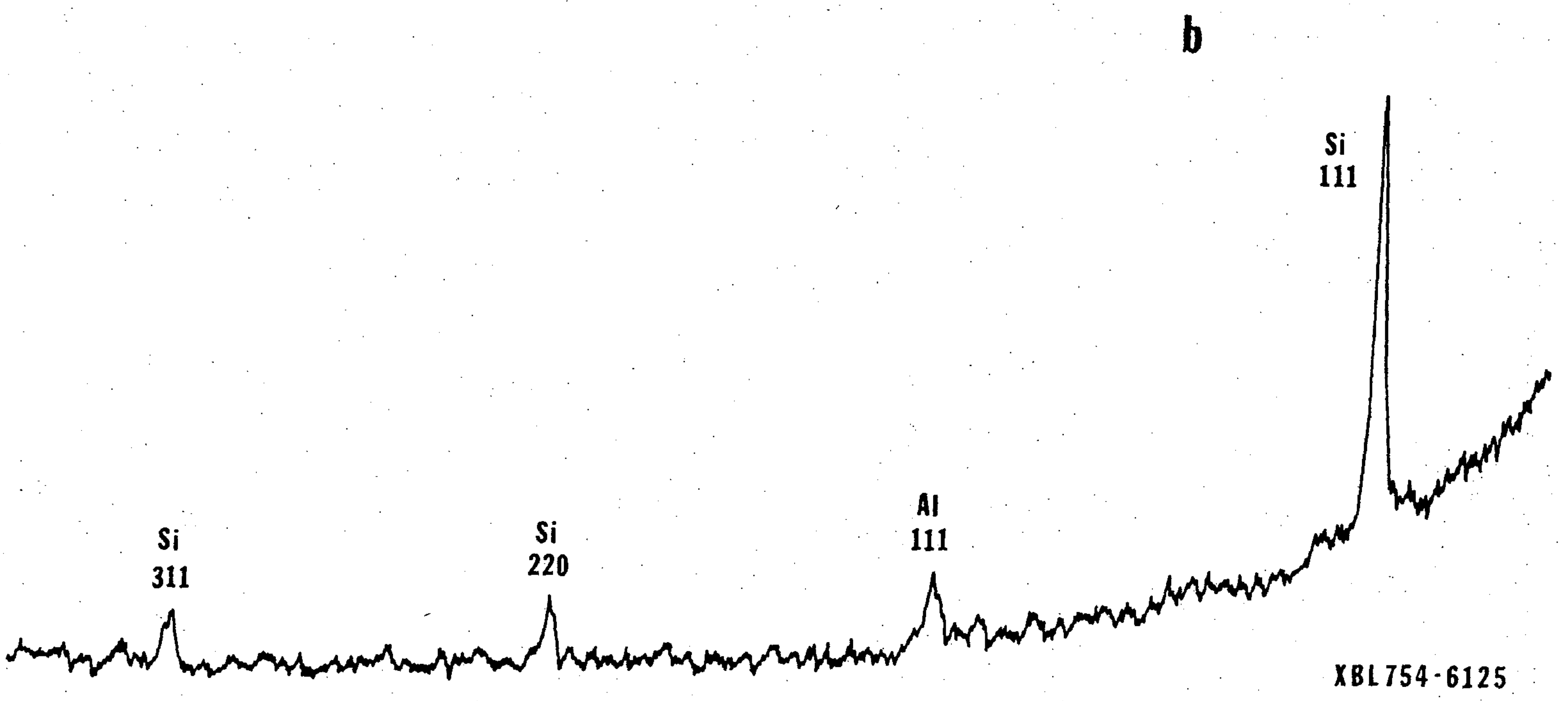
Fig. 1. X-ray diffraction patterns for the silicon films deposited on (a) graphite, and (b) quartz, using the Si-Al-Si sandwich coating technique.

Fig. 2. Auger depth profiles for the silicon films deposited on (a) graphite, and (b) quartz, using the Si-Al-Si sandwich coating technique. Sputtering rate of the silicon films is ca 50Å/min.



XBL 754-6126

Fig. 1a



XBL754-6125

Fig. 1b

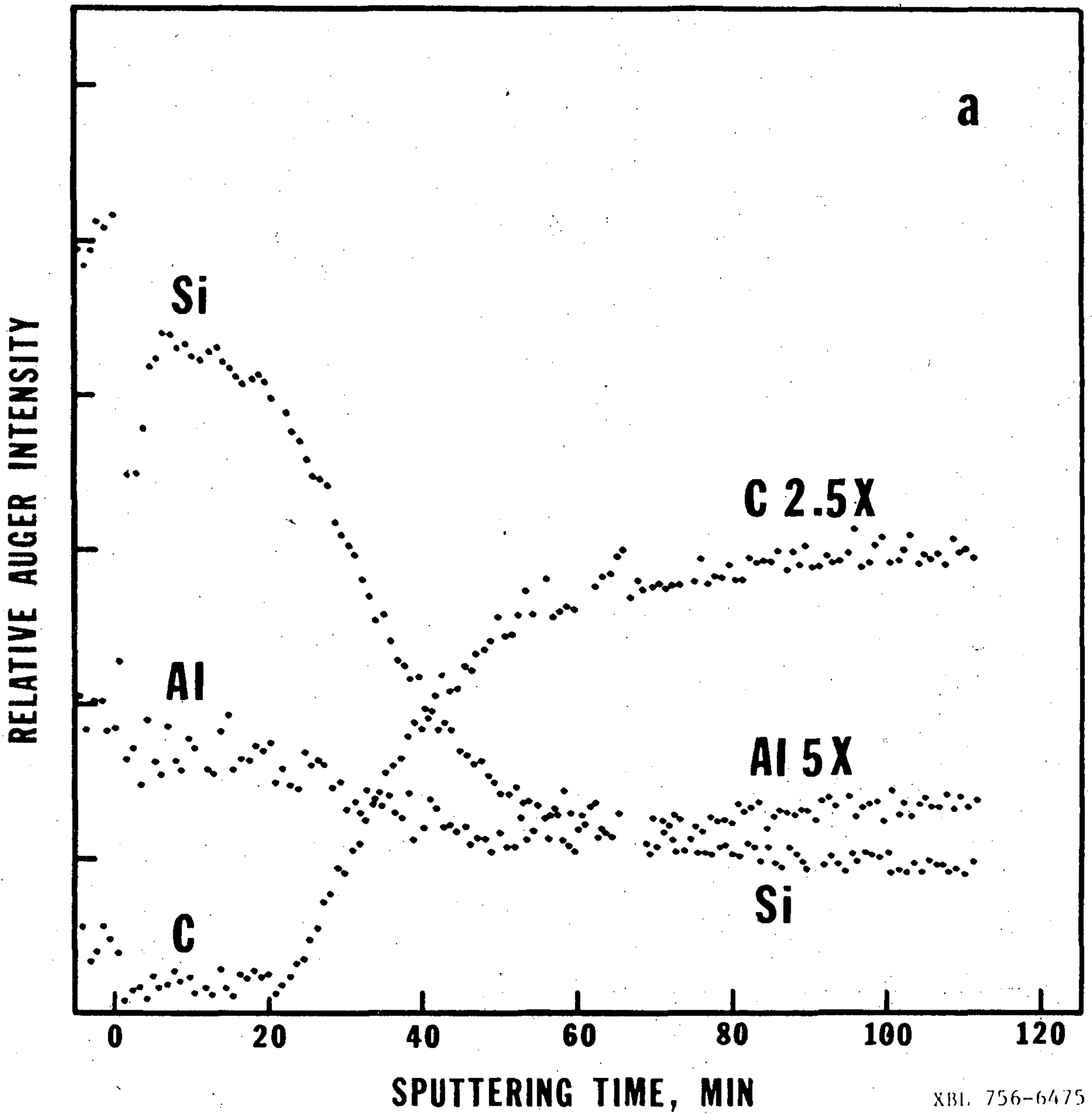

a
Si
C 2.5X
Al
Al 5X
Si
C
RELATIVE AUGER INTENSITY
0
20
40
60
80
100
120
SPUTTERING TIME, MIN
XBL 756-6475

Fig. 2a

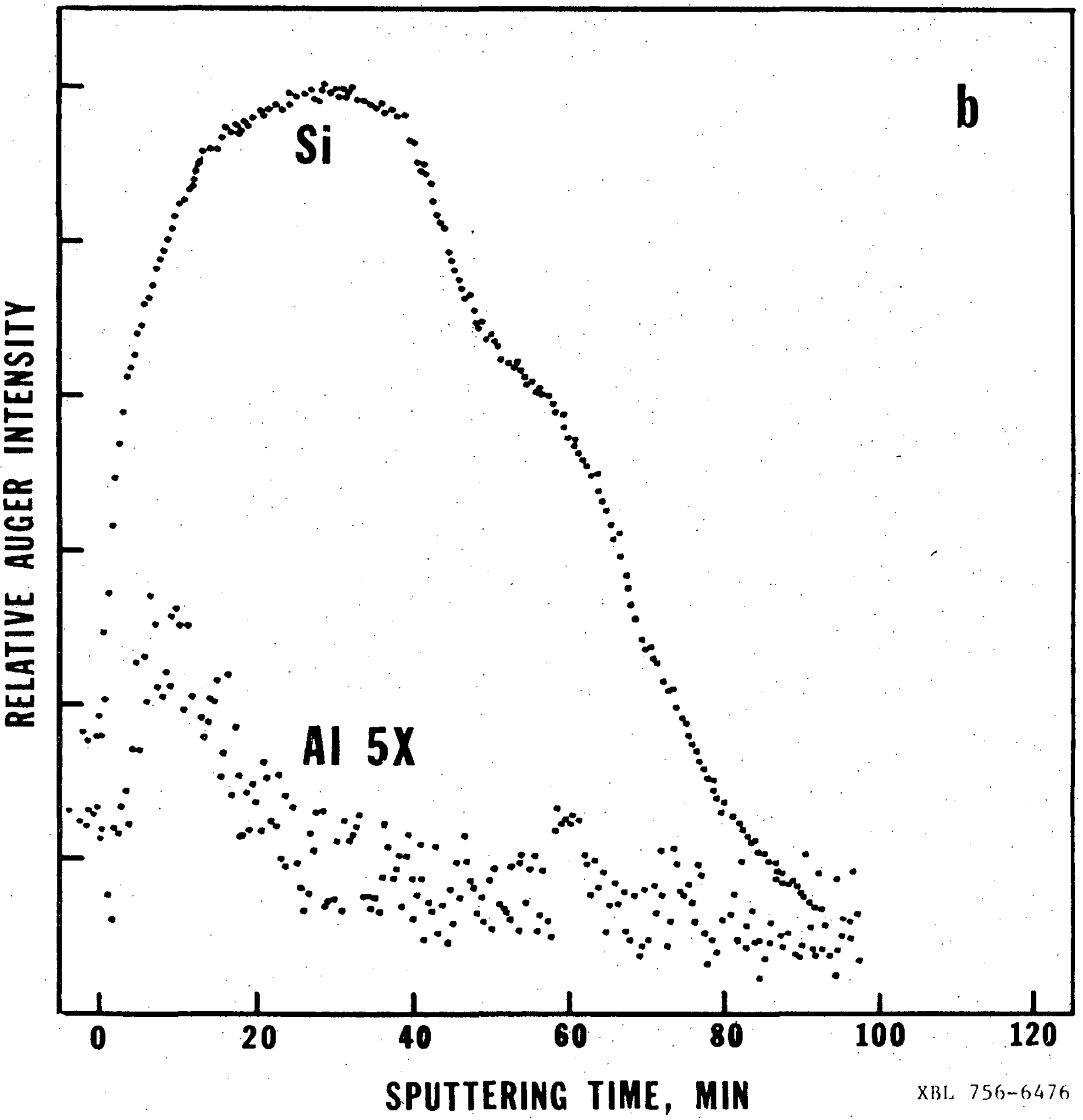

b
Si
Al 5X
RELATIVE AUGER INTENSITY
0
20
40
60
80
100
120
SPUTTERING TIME, MIN
XBL 756-6476

Fig. 2b

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720