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FINAL REPORT TO
NAVAL RESEARCH LABORATORY

KINETICS OF SILICIDE FORMATION
IN ARTIFICIALLY MULTILAYERED
CHROMIUM-AMORPHOUS SILICON THIN FILMS

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May 1991

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This report concerns a research program involving a collaborative study between Johns Hopkins and the Naval Research Laboratory. Silicide formation in multilayered thin films of chromium and amorphous silicon was investigated by differential scanning calorimetry. Details can be found in the preprint for a paper in press (scheduled to appear in the July 22 issue of Applied Physics Letters).

A summary of results is given below:

1. The kinetics of silicide formation during interfacial reactions between chromium and amorphous silicon was found to be interface reaction limited (linear rate law). This is the first time this DSC technique has been used to identify interface limited kinetics.
2. The rate constant v , corresponding to an interface velocity, was calculated to be $v = 7.5 \times 10^7 \exp[-(2.6 \text{ eV}/kT)] \text{ m/sec}$.
3. Unlike in several previously reported studies involving metal-amorphous silicon reactions, an explosive reaction could not be induced in the chromium-amorphous silicon system.

This work was supported at Johns Hopkins by the Office of Naval Research under Contract No. N00014-89-K-2016.

Kinetics of Silicide Formation in Chromium-Amorphous Silicon
Multilayered Films

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ABSTRACT

Silicide formation in multilayered thin films of chromium and amorphous silicon was investigated by differential scanning calorimetry (DSC). The DSC traces gave a large main peak that was associated with the growth of the silicide. The growth kinetics followed a linear rate law, with an activation energy of 2.6 eV and a pre-exponential factor of 7.5×10^7 m/sec for the rate constant. An explosive silicide reaction, observed in other metal-silicon multilayered films, could not be induced in this system.



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PACS numbers: 61.50.Cj, 64.70.Kb, 81.30.-t, 82.20.Pm
Submitted to Applied Physics Letters, March, 1991

Recently, differential scanning calorimetry (DSC) has been used to study the kinetics of amorphous phase formation¹ and metal silicide formation²⁻⁵ in multilayered thin films. In this letter, an investigation of the kinetics of silicide growth in chromium/amorphous silicon multilayered thin films using differential scanning calorimetry is presented. It is shown that the growth rate is interface (reaction rate) limited, and an activation energy and pre-exponential for the reaction rate constant are given.

The experimental procedure used in the present study closely paralleled the method used by Clevenger et al.². Multilayered thin films were prepared by sequential electron beam evaporation of chromium and silicon onto microscope slides coated with photoresist that was about 2 μm thick. X-ray diffraction analysis of the deposited films indicated that the chromium was polycrystalline and the silicon was amorphous. As is discussed below, analysis of the reaction kinetics indicates there was also an interfacial layer of (amorphous) silicide, as has been observed in as-deposited nickel-amorphous silicon⁶ and vanadium-amorphous silicon⁷ multilayered thin films. The ratio of the layer thicknesses, silicon to chromium, was about 3.3 to 1, which gave an overall atomic composition ratio of silicon to chromium of 2 to 1. This ratio was chosen because the silicide to form during interfacial reactions of chromium and silicon is⁸⁻¹⁰ CrSi_2 . Though this is based on reactions involving crystalline silicon, it was expected (and, as discussed below, later confirmed) that the same phase would form in the present study. A series of films with nominal chromium-silicon layer thicknesses

of 1.9 nm-6.2 nm, 4 nm-13.2 nm, 8 nm-26 nm, and 23.5 nm-76.5 nm (corresponding to bilayer periods of 8.1, 17.2, 34 and 100 nm, respectively) were prepared. Each film was composed of ten layers, and therefore the total film thickness was five times the bilayer period. The films were removed from the substrates by dissolving the photoresist in acetone, and were heated in a Mettler DSC 30 Differential Scanning Calorimeter at rates of 5 to 50°C/min over a temperature range of 70 to 600°C. X-ray diffraction analysis of the reacted films gave diffraction patterns consistent with the presence of crystalline CrSi₂.

A typical DSC trace is shown in Figure 1, generated from a 80 nm Cr-260 nm Si film (bilayer period $\lambda = 34$ nm) heated at a rate of 20°C/min. There is a large peak associated with the growth of the silicide. The sharp drop-off at the peak temperature was indicative of the end of the reaction, which occurred when each silicide layer had grown to a thickness of half the bilayer period λ . For a given heating rate, the peak temperatures increased for increasing bilayer period, due to the longer time needed for the silicide layer to grow to a final thickness $\lambda/2$.

In most traces a much smaller peak at lower temperatures (about 285°C in Figure 1) preceeded the main peak. Similar peaks have been seen in DSC studies of interfacial reactions in nickel-amorphous silicon^{2-4,9} and vanadium-amorphous silicon multilayered films¹⁰. This smaller peak has been attributed to the nucleation of the crystalline silicide^{9,10}. An issue of considerable interest has been whether the kinetics of nucleation¹⁰ or of growth¹¹ are responsible for determining which

of several possible silicide phases first appears during metal-silicon reactions. It has been argued that multiple peak DSC scans for the nickel-amorphous silicon system can be explained only if nucleation barriers are responsible for determining the first phase formed¹⁰. Nucleation barriers as the mechanism for first phase formation has been invoked to explain the first phase to form in multilayered nickel-amorphous silicon thin films (Ni_2Si)¹⁰ and in nickel implanted amorphous silicon thin films (NiSi_2)¹². The presence of multiple peaks in most of the DSC traces of this study may also be evidence of nucleation barriers determining first phase formation in the chromium-amorphous silicon system.

The growth kinetics of interfacial reactions in multilayered thin films were analyzed using peak temperatures obtained from DSC scans in the following manner^{1-5,9,13}. For the case of interface limited growth, the rate of change of the thickness x of the silicide layers is given by^{9,10}

$$dx/dt = v, \quad (1)$$

where v is a rate constant corresponding to the interface velocity. The rate constant is generally expressed in the Arrhenius form⁸

$$v = v_0 \exp(-Q/kT), \quad (2)$$

where Q is an activation energy, k is Boltzmann's constant, T is the absolute temperature, and v_0 is a temperature independent

constant. Solving for x in Equation (1), and allowing for a time dependence of the temperature during a DSC scan gives

$$x - x_0 = v_0 \int \exp(-Q/kT) dt = (v_0/H) \int \exp(-Q/kT) dT, \quad (3)$$

where $H = dT/dt$ is the DSC heating rate and x_0 is the thickness of a silicide layer in the as-deposited film. For a film that is completely reacted, we can write Equation (3) in the form

$$\lambda/2 - x_0 = (v_0/H) \int_{T_0}^{T_p} \exp(-Q/kT) dT, \quad (4)$$

where T_0 and T_p are the initial and peak temperatures, respectively. The growth rate for a diffusion controlled process can be written as^{1,2}

$$dx/dt = D/x, \quad (5)$$

where the rate constant D can be taken as an effective interdiffusivity. Proceeding in a manner similar to that used to derive Equations (1) to (4) gives

$$(\lambda/2)^2 - x_0^2 = (2D_0/H) \int_{T_0}^{T_p} \exp(-Q/kT) dT, \quad (6)$$

where D_0 is a temperature independent constant.

The kinetics of the silicide reaction was studied by measuring peak temperatures scans using the same heating rate on samples with different bilayer periods. An attempt was made to

obtain the best linear fit to Equations (4) and (6) by using two plots: $\int_{T_0}^{T_p} \exp-(Q/kT) dT$ versus $\Lambda/2$ and $\int_{T_0}^{T_p} \exp -(Q/kT) dT$ versus $(\Lambda/2)^2$, where Q was an adjustable parameter. From these fits, a pre-exponential constant and an as-deposited reacted layer thickness x_0 were obtained. This procedure was carried out using peak temperatures of DSC scans for 10 and 20°C/min heating rates. For the 10°C/min heating rate, the best fit was obtained for both plots with a Q of 2.7 eV, while the best fit for the 20°C/min heating rate was obtained using a value of $Q = 2.6$ eV. In both cases, the linear kinetics plots gave better fits than the parabolic kinetics plots; in addition, the linear kinetics plots gave a reasonable value for x_0 of about 3.5 nm, while the parabolic kinetics plots gave negative values for x_0 , even when they were fit using a range for Q of 2.4 to 2.9 eV. Thus, the conclusion is that the growth of the silicide was governed by interface limited kinetics. This is the first time this type of DSC investigation has been used to characterize interface limited silicide growth. It is interesting to note that while most interfacial silicide reactions involving a transition metal and crystalline silicon are diffusion limited, the chromium-crystalline silicon reaction is interface limited⁸⁻¹⁰.

Figure 2 shows a plot of $\int_{T_0}^{T_p} \exp -(Q/kT) dT$ versus $\Lambda/2$ for a heating rate of 20°C/min using a value for Q of 2.6 eV; a similar plot was obtained for the 10°C/min heating rate. From the slope, a value of $v_0 = 7.5 \times 10^7$ m/sec was obtained. As a comparison, studies involving interfacial reactions of chromium with crystalline silicon in the temperature range 450 and 500°C gave values¹⁰ of Q between 1.5 to 1.7 eV and values for v of

between 0.7 to 3.7×10^{-10} m/sec. Using Q and v_0 obtained in this study gives values of v of 0.60×10^{-10} m/sec and 8.9×10^{-10} m/sec for temperatures of 450 and 500°C , respectively. It is interesting to note that for this temperature range, the rate constants for reactions involving amorphous and crystalline silicon are extremely close despite the relatively large difference in Q .

It was also possible to calculate the activation energy of the silicide reaction by measuring, for samples of the same bilayer period, peak temperatures of DSC traces for different heating rates using an analysis given by Kissinger¹⁴: the slope of $\ln (H/T_p)$ vs. $1/T_p$ is $-Q/k$. Kissinger plots for each bilayer period were made and gave an activation energy of 2.7 ± 0.3 eV, which is in agreement with the value of Q calculated above.

For many multilayered metal-silicon thin films, it was found that an explosive reaction could be initiated by mechanical impact and other stimuli^{2-5,15-17}. Such explosive silicide formation is similar to explosive crystallization in amorphous thin film systems such as Ge^{18} and CdTe^{19} . Several attempts to induce this type of reaction in the films used in this study were made, but an explosive reaction was not observed.

In conclusion, differential scanning calorimetry has been used to analyze growth kinetics of silicide in multilayered thin films. It was shown that the growth rate followed a linear rate law corresponding to interface limited kinetics, and the rate constant was calculated to be $v = 7.5 \times 10^7 \exp -\{(2.6 \text{ eV})/kT\}$ m/sec. An explosive silicide reaction in these films could not be induced.

ACKNOWLEDGEMENTS

The authors thank Wayne Moore for preparation of the samples, and Professor D.O. Cowan, K. Araki, and Michael Mays for help with the calorimetry. This work was supported at Johns Hopkins by the Office of Naval Research under contract N00014-89-K-2016.

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FIGURE CAPTIONS

Figure 1. DSC trace for a film of bilayer period $\Lambda = 34$ nm heated at a rate of $20^{\circ}\text{C}/\text{min}$.

Figure 2. Plot of $\int_{T_0}^{\bar{T}_p} \exp -(Q/RT) dT$ as a function of $\Lambda/2$ for samples heated at a rate of $20^{\circ}\text{C}/\text{min}$ using $Q = 2.6$ eV.

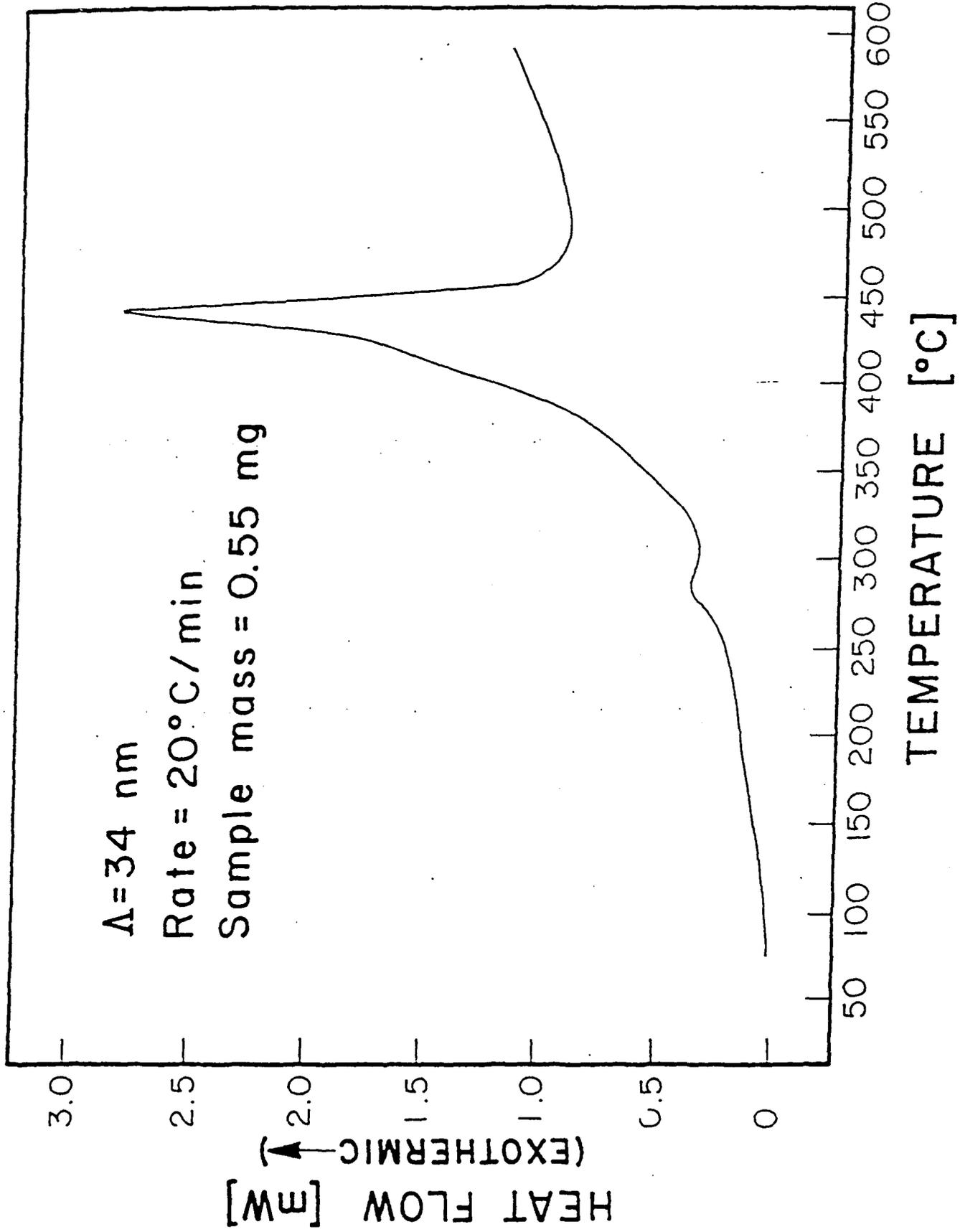


Figure 1.

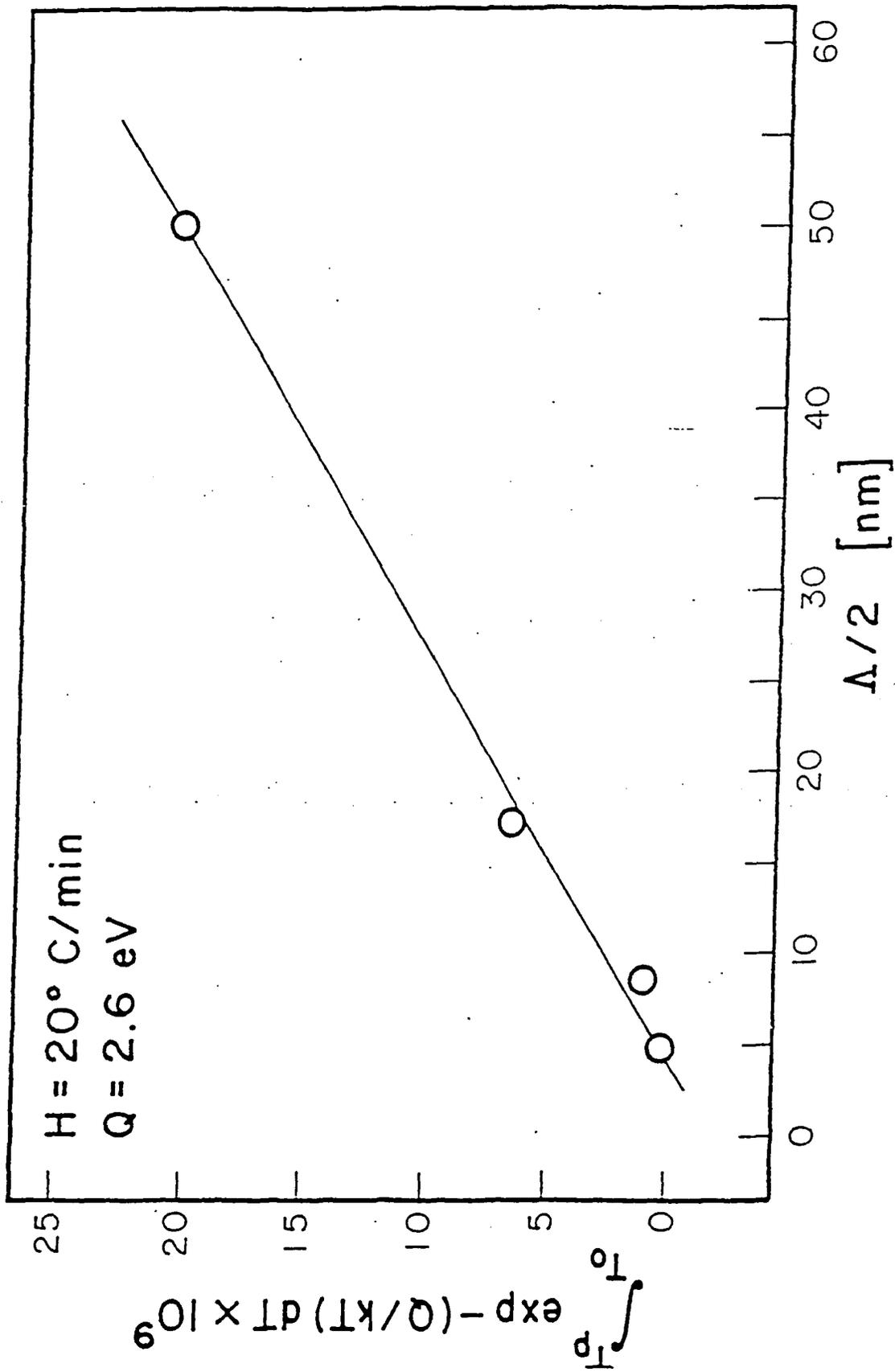


Figure 2.