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Analysis of Oxygen Precipitation in Silicon

by Infrared Absorption

by

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Abstract

Infrared absorption measurements have been used to study the precipitation rate of oxygen in silicon and the conversion of interstitial oxygen to silicon dioxide. For this purpose slugs of silicon were heated up to 200 hours at 1050 C and 1250 C respectively. The oxygen precipitation rate at 1050 C was found to be diffusion limited and at 1250 C reaction limited. At both temperatures the interstitial oxygen approached equilibrium values. The larger value occurring at the higher temperature. This result is consistent with the observation that silicon dioxide is dissolved in silicon and oxygen returned to interstitial lattice sites at temperatures approaching the melting point of silicon. The precipitation rate was found to be independent of the silicon dislocation density and of material from different crystal growers. The conversion rate of interstitial oxygen into silicon dioxide varies widely with oxygen concentration and temperature, this explains the well known dependence of leakage currents in pn junctions on details of their processing. The use of infrared measurements will also have application.

in evaluating the effectiveness of heat treatments on silicon crystals. By using infrared measurements to determine the amount of oxygen remaining in interstitial lattice sites after heating the magnitude of donor effects can be calculated.

Introduction

Oxygen in silicon is a dopant unintentionally entering melt grown (Czochralski) crystals during growth. Large quantities of oxygen are dissolved in the molten silicon from its quartz crucible and incorporated into the growing crystal. Typical levels of oxygen encountered in Czochralski grown silicon crystals range from 10 to 50 ppm atomic. These levels usually exceed the concentration of intentional dopants, while crystals prepared by the floating zone technique generally contain less than 1 ppm atomic of oxygen. Oxygen in interstitial lattice sites is noted for donor formation(1,2). These donors can obscure the resistivity of the material due to intentional dopants. To eliminate these oxygen donors, the crystals are heat treated and oxygen converted to silicon dioxide before the resistivity is evaluated. Above approximately 1000 C the interstitial oxygen begins to precipitate as silicon dioxide that has been associated with undesirable leakage currents in pn junctions. Batavin (14) has shown that silicon dioxide precipitates reduce the breakdown voltage of a pn junction by as much as

50%.

Thus a study of factors affecting the precipitation of oxygen is required in evaluating heat treatments of silicon crystals. Such information is also useful for determining oxygen precipitation caused by a specific device processing sequence that will affect pn junction leakage currents. The purpose of this investigation is to establish the use of infrared absorption measurements as a tool for observing the precipitation of oxygen. Additionally the precipitation rate was examined as a function of temperature, dislocation density, and crystal grower.

Physical Background of Heat Treating

In the heat treating of silicon as discussed by Baker (11) and other workers a low temperature range is commonly accepted from 400 C to 700 C. Heating the silicon in the range from 400 C to 500 C produces donors due to the formation of silicon tetraoxide complexes. Heating the material in the 500 C to 700 C range destroys the donor complexes and returns the oxygen to interstitial lattice sites. But the effect of the heat treatment in the 500 C to 700 C range is not permanent, since reheating the silicon between 400 C and 500 C will again produce donors. The amount of oxygen convertible to silicon tetraoxide by heating depends on interstitial oxygen content, temperature, and heating time. For example, silicon with 45 ppm interstitial oxygen content heat for 10 minutes at 450 C will convert 0.1 % of the oxygen (11), while a similar sample with 30 ppm oxygen heated for 100 hours at 450 C converted 14% of the oxygen into silicon tetraoxide. The heat treatment in the 500 C to 700 C range is especially useful for determining the resistivity of a sample due to intentional

dopants as arsenic or boron; however, this treatment is reversible.

Above 1000 C the equilibrium phase for oxygen in silicon is silicon dioxide; however, at temperatures approaching the melting point of silicon (1416 C) silicon dioxide is dissolved and oxygen returned to interstitial lattice sites. Silicon dioxide will not behave as a donor, and is also stable between 400 C and 700 C. Thus, a silicon sample having all its oxygen precipitated does not show any donor effects after heating between 400 C to 500 C.

During crystal growth most of the oxygen is incorporated into interstitial lattice sites (11). Some of the oxygen is present as silicon tetraoxide. But as mentioned before a heat treatment can modify the initial status of the oxygen.

Background of Infrared Measurement

Infrared analysis of interstitial oxygen in silicon was first reported by Kaiser and Keck (1), but many years passed before a quantitative relation between absorption coefficient and interstitial oxygen content was developed. This relation is described in ASTM document F-121 (6), which also provides guidelines for the measurement. A brief outline of this document is contained in Appendix A. An oxygen interstitial line at 1106 wavenumbers is very strong and easily observed at room temperature for concentrations of 2 to 63 ppm, the latter figure corresponding to the solid solubility of oxygen in silicon (7). Other interstitial oxygen lines(1) are observable in the 20 to 30 micron region of the spectrum at low temperatures (20 K). Thus the 1106 wavenumbers line observable at room temperature is most easily used in routine measurements of large numbers of silicon samples. Shown in figure 2 is a spectrum of a typical slug used in this study prior to any heat treatments.

Experimental

A Perkin Elmer 457 infrared grating spectrometer was used for the analysis. It has a built in chart recorder so that a permanent copy of the spectrum is recorded with each measurement. Its resolution of 2.0 wavenumbers at 1000 wavenumbers is adequate to observe the 1106 wavenumbers oxygen line having a line width of 32 wavenumbers. A scan speed of 200 wavenumbers per minute was used. An ordinate expansion of 2.5 was employed to easily observe small changes of the spectrum during heat treatments. The scan speed of 200 wavenumbers per minute allowed recording of the spectrum accurately. A faster speed shifted the position of the line and its full depth was not developed. To determine the repeatability of the measurement a silicon slug was measured periodically throughout the course of the study. The oxygen content was nominally 36 ppm and its repeatability over a three month period was within $\pm 4\%$ three sigma limits. At a lower concentration of 2 ppm the repeatability was within $\pm 10\%$ three sigma limits.

The slugs were heat treated in a Thermco Brute

resistance heated furnace having a 15 inch hot zone. Its temperature control is typically ± 2 C over two months. Temperatures were measured with a platinum-rhodium thermocouple using a Doric thermocouple thermometer that is accurate to within ± 5 C. The temperatures 1050 C and 1250 C were chosen because they represent typical processing temperatures.

After removal from the furnace the slugs typically had an oxide of 5000 to 9000 angstroms in thickness. It was measured utilizing infrared interference fringes (8). The oxide indicated the presence of oxygen and/or water vapor in the nitrogen ambient during the heat treatment cycle. Figure 1 is a sketch of the furnace system. The entry points for oxygen and water vapor are shown. A moisture monitor in the nitrogen purge line normally indicates a water content of 1 ppm. The effect of this contamination was evaluated in the following fashion. A float zone slug which showed no measureable oxygen was heated for 50 hours at 1250 C in pure oxygen. The solid solubility of oxygen at 1250 C is approximately 20 ppm and the diffusion length at this time

and temperature is 7 mils. This considerable amount of oxygen diffused into a 150 mil slug at 1250 C had only a small effect on the spectrum, corresponding to an equivalent of only 1 ppm oxygen in the float zone slug after the oxygen treatment. Thus, the contamination of the nitrogen ambient with oxygen and/or water vapor did not affect the spectra of the slugs used in this study.

Silicon material for the experiment was gathered from the seed end of as grown ingots. The slugs were cut to a nominal thickness of 150 mils. This thickness produces an absorption line that covers 80% to 20% transmission on the spectrophotometer chart. After cutting, the slugs were ground to produce a sample with parallel sides. Two kinds of slug polish were evaluated. The first was a polish that used a Syton lapping compound to produce a specular surface. This polish conforms to the requirements of the ASTM document (Appendix A). The second was a chemical polish commonly known as 533 consisting of 5 parts nitric acid, 3 parts hydrofluoric acid and 3 parts acetic acid. Both polishing procedures were found to be of equal quality with respect to the in-

frared measurement. Once the chemical polish was qualified it was used on the majority of samples.

Silicon for the experiment was obtained from two different crystal growers. This served two purposes: material grown on various machines provided a wider range of oxygen levels for study, and secondly any influences on the precipitation rate due to machine type could be examined. Also material dislocation density was investigated. Two dislocation densities were considered. The first, known as standard material, had a dislocation density between 2000 to 5000 etch pits per square centimeter, the second kind, referred to as dislocation free, had an etch pit count of less than 500 etch pits/centimeter squared. These etch pit densities were evaluated using the ASTM procedure outlined in Appendix B.

The slugs were heat treated and measured every 25 hours up to 50 or 100 hours. After that the time interval between measurements was increased to 50 or 100 hours as the changes of the spectra became smaller. The total time span was limited to 200 hours because an initial study showed no significant

changes of the spectra between 200 and 400 hours.

The slugs were rapidly inserted and withdrawn from the furnace at the various temperatures. A quartz paddle supported the slugs during the heat treatments. After removal from the furnace the slugs were allowed to cool to room temperature while remaining on the paddle. The cooling process required approximately 30 minutes. Prior to the infrared measurement, the slugs were dipped in hydrofluoric acid to remove the oxide.

Then the samples were measured on the spectrophotometer and the interstitial oxygen content determined according to the ASTM procedure (Appendix A). For purposes of this study the precipitation rate has been defined as the time rate of the interstitial oxygen content as evidenced by the infrared measurements.

Results and Discussion

Figure 2 is a spectrum of a typical slug prior to any heat treatment. This spectrum is to be compared with the spectra obtained after heating at 1050 C and 1250 C, as detailed in figures 3 and 4. Figure 3 is the spectrum of a typical slug after a 200 hour heating at 1050 C. Notable first is the broadening of the line at 1106 wavenumbers similar to that of silicon dioxide glass (Figure 5), and second the appearance of another silicon dioxide band at 1228 wavenumbers. This band is not present in silicon dioxide glass (films), but was associated with silicon dioxide precipitates in silicon by Smakula(12), who heated material at 1000 C. A spectrum from his work is presented in figure 6.

The spectrum of a typical slug after 200 hours heating at 1250 C is presented in figure 4. It shows only one line at 1106 wavenumbers similar to that of the starting spectrum (Figure 2). The line width broadened from the original value of 32 wavenumbers to 50 wavenumbers during the course of the heat treatment. By comparison, the line width broadened to 80 wavenumbers from 32 wavenumbers with heating

at 1050 C. The 1228 wavenumbers band is missing in the spectrum of the sample heated at 1250 C.

The results of the infrared measurements versus time for the two temperatures are shown in figures 7 and 8. At 1050 C the precipitation of oxygen in the high concentration samples rapidly approached an equilibrium value. Lower concentration slugs attained equilibrium more slowly. This indicates a diffusion limited condition at this temperature. The precipitation at 1250 C proceeded more slowly as is seen in comparing figures 7 and 8.

Interpretation of the spectra is as follows. The spectrum obtained after heating at 1050 C is a combination of the line at 1106 wavenumbers plus a spectrum due to silicon dioxide, whose band is centered at 1080 wavenumbers. Also present in the spectra at 1228 wavenumbers is the band due to silicon precipitates. Spectra obtained after heating a 1250 C shows no pronounced effects due to silicon dioxide. Two reasons for this difference can be imagined. First the 1250 C spectrum contains less precipitation as noted by the higher equilibrium

value of interstitial oxygen in figure 8. Thus, with less silicon dioxide being present less absorption due to silicon dioxide can be expected. Secondly above 1180 C in quartz silicon monoxide is a stable form; thus some of the interstitial oxygen is converted to silicon monoxide rather than to silicon dioxide.

Another interesting aspect of the heat treatments were the equilibrium values of interstitial oxygen obtained at each temperature. The value at 1050 C is about 12.5 ppm compared with 22.0 ppm at 1250 C. The higher value at 1250 C agrees with the fact that at this temperature silicon dioxide is dissolved in silicon and oxygen returned to interstitial lattice sites. The existence of interstitial oxygen at both temperatures indicates that the oxygen precipitation is not completed due to competing reactions to dissolve the silicon dioxide. At 1050 C existed a diffusion limited condition with the reaction to form silicon dioxide dominating, whereas at 1250 C a reaction limited condition was present due to the reaction to dissolve silicon dioxide dominating. Thus at 1250 C with the reaction to dissolve silicon

dioxide predominating, it is harder to obtain equilibrium.

One set of slugs was processed at 1050 C that contained both standard dislocation density and dislocation free material. After a heat treatment of 100 hours with measurements made at the 50 and 100 hour marks, the dislocation free material behaved similar to the standard material. At the conclusion of the heat treatment the dislocation free material was sirtl etched and inspected. Some additional dislocations did form in the outer 3 millimeters of the slugs. This was not considered significant as no measurements were made at the edge of the slugs.

Material from two types of crystal growers were included in the study and no differences due to machine type were noted.

Conclusions

The use of infrared measurements as a tool to study the precipitation of oxygen in silicon has been demonstrated. The measurement was able to detect changes in the spectrum due to interstitial oxygen precipitating to silicon dioxide. By measuring the decrease of the interstitial oxygen with heat treatments the amount of oxygen remaining in interstitial lattice sites is determined.

One application of the infrared measurement is the quantitative evaluation of heat treatments on silicon crystals. Knowing the oxygen remaining in interstitial lattice sites after a heat treatment, the amount of donors that will be formed with heating in the 300 C to 500 C range can be estimated. For example a silicon sample with a 45 ppm interstitial oxygen content will produce 1.2×10^{15} donors/cc with heating at 450 C for 10 minutes. If this sample is then heated for 200 hours at 1050 C such that 12 ppm of interstitial remains the same low temperature heat treatment produces only 3.0×10^{11} donors/cc.

The experimental results show the rate of precipita-

tion as a function of oxygen concentration, temperature and duration of heat treatment. Therefore the leakage currents of pn junctions in semiconductor devices can be expected to depend on the specific processing times and temperatures.

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Appendix A

Outline of ASTM document F-121 for Oxygen Content Determination in Silicon by Infrared Absorption

1. The sample must have a resistivity greater than .01 ohm-cm.
2. The oxygen content of the sample should be in the range 50 ppb to 63 ppm.
3. The spectrophotometer used for the measurement must have a resolution of at least 5 wavenumbers at 9 microns. The spectrum obtained from the instrument should have a line width of 32 wavenumbers .
4. For Czochralski grown samples the thickness should be approximately 2 to 4 millimeters .
5. For float zone prepared samples the sample thickness should be approximately 10 millimeters.
6. Prepare the sample in any manner which produces a specimen with optically flat and parallel surfaces.
7. Calculate the absorption coefficient from the spectrum of the sample and the sample thickness.

8. The oxygen content is obtained by multiplying the absorption coefficient by 9.63.

9. Single instrument precision for this measurement is expected to be at least 3% one sigma.

Appendix B

Outline of ASTM Document F 47 Test for Perfection of Silicon by Preferential Etch Techniques.

1. The procedure is applicable to dislocation densities in the range 0 to 100,000 per centimeter squared.
2. The method is limited to material with a [111] orientation.
3. The test sample must be at least 1 millimeter thick.
4. Prepare the test sample by lapping one side with No. 600 alumina to remove at least .05 millimeters of material.
5. Wash and rinse the sample. The surface should appear uniform in finish and free of any scratches.
6. Place the sample in a beaker and add the dislocation etch.
7. The dislocation etch consists of 600 ml hydrofluoric acid, 300 ml nitric acid, and 28 grams of copper nitrate.

8. Be sure to observe all acid handling rules when preparing and using the etch.
9. Keep the sample in the etch until it develops a chemically polished surface. Then dilute the etch solution with water to stop the reaction.
10. Dry the sample.
11. Examine the sample using a microscope with 200 power magnification to determine if etch pits have formed. If pits have not formed re-etch the sample.
12. Reduce the magnification to 150 and count the etch pits in the field of view.
13. Examine several area on the sample.
14. From the etch pit counts and knowing the area of the field of view the dislocation density can be calculated.

Vita

Charles W. Pearce was born to Mary and Herman E. Pearce on May 22, 1947 in Philadelphia, Pennsylvania. After completing his primary and secondary education in the public schools of King of Prussia, Pennsylvania, he enrolled in the electrical engineering curriculum at the University of Nebraska. While attending the university he was honored with membership in the engineering honoraries Eta Kappa Nu and Sigma Tau. He graduated in June of 1969 with a Bachelor of Science in Electrical Engineering. In September of 1969 he entered Lehigh University in pursuit of a Master of Science degree in Electrical Engineering.

In July of the same year Mr. Pearce started his association with the Allentown Works of Western Electric as an engineer in the Semiconductor Materials Engineering group. He was promoted to Planning Engineer in 1970. For the past four years Mr. Pearce has been involved with the measurement of the electrical and optical properties of semiconductors. He is an active member of The American Society for the Testing of Materials and has co-authored the fol-

Following paper, Langer, P.H. and Pearce C.W., "Epitaxial Resistivity ", Journal of Testing and Evaluation, Vol. 5, 1973, p. 305. Mr. Pearce and Ellen, his wife of seven years, currently reside in Allentown, Pennsylvania, with their two children Elizabeth and Adam.

FURNACE SETUP

HOT ZONE

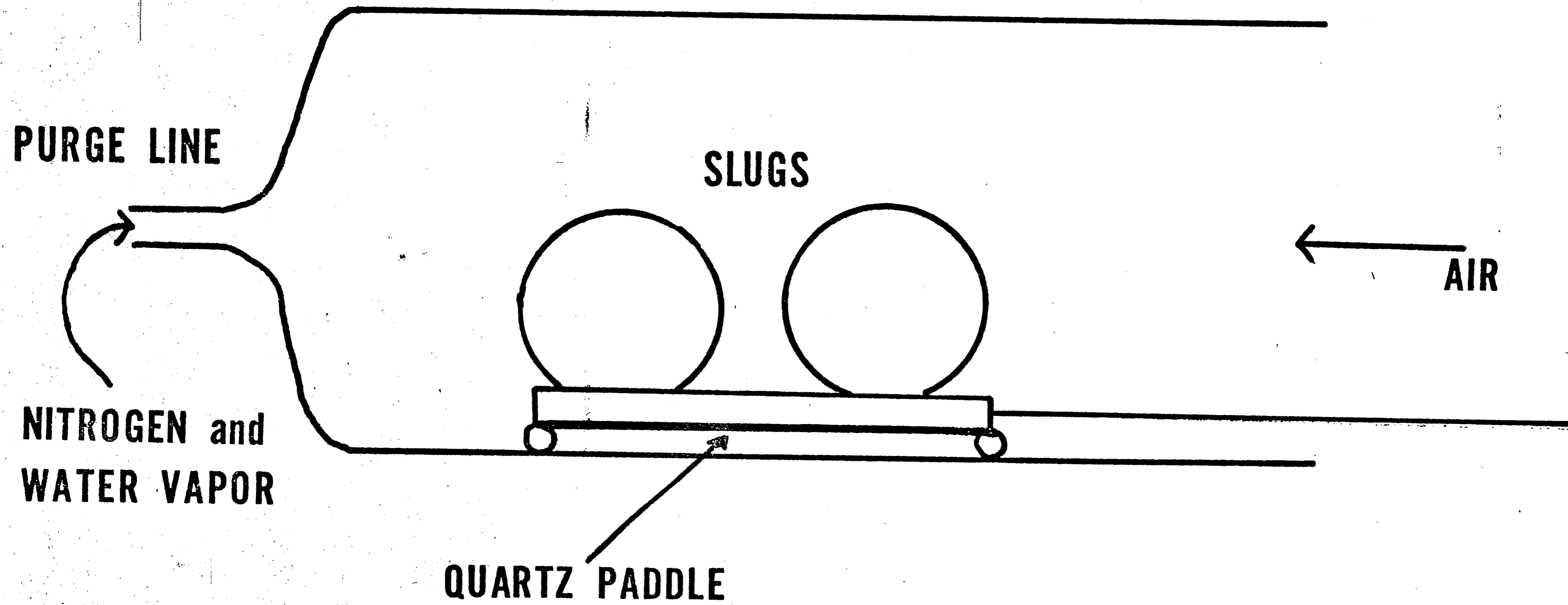


FIGURE 1

TYPICAL SPECTRUM OF SLUG
AFTER 200 HOURS AT 1050 C

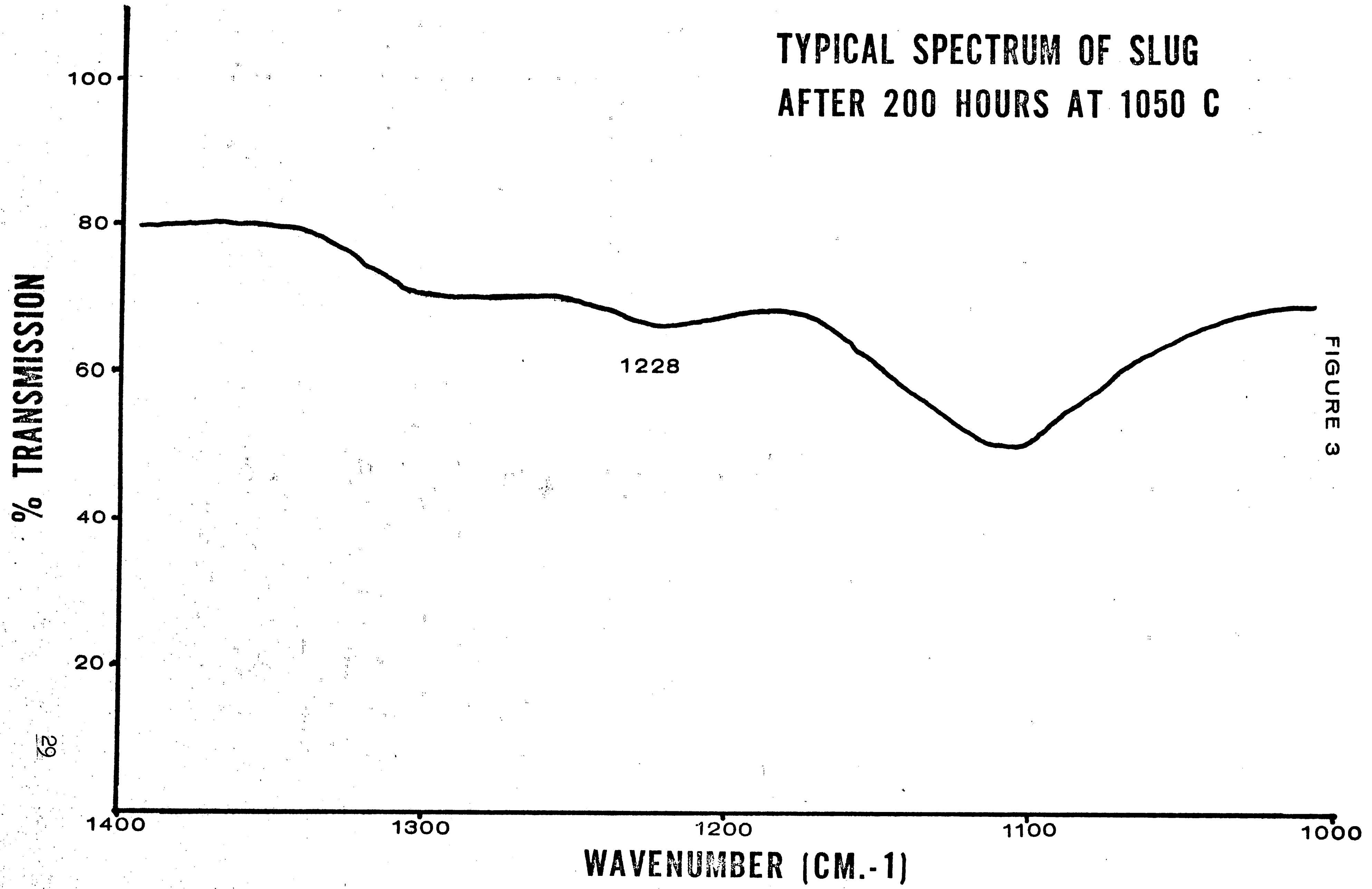


FIGURE 3

TYPICAL SPECTRUM OF SLUG
BEFORE HEAT TREATMENT

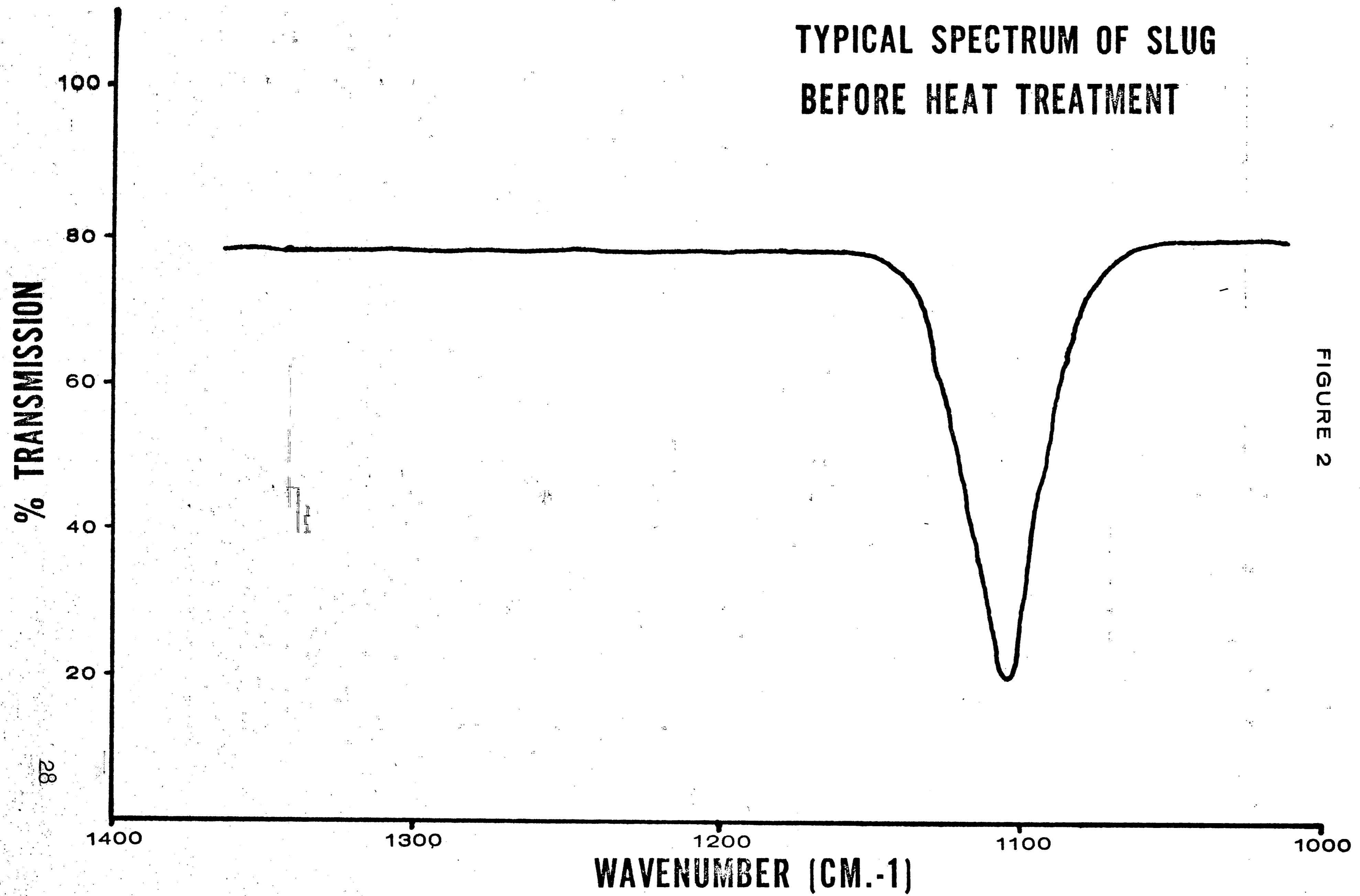


FIGURE 2

7

TYPICAL SPECTRUM OF SLUG
AFTER 200 HOURS AT 1250 C

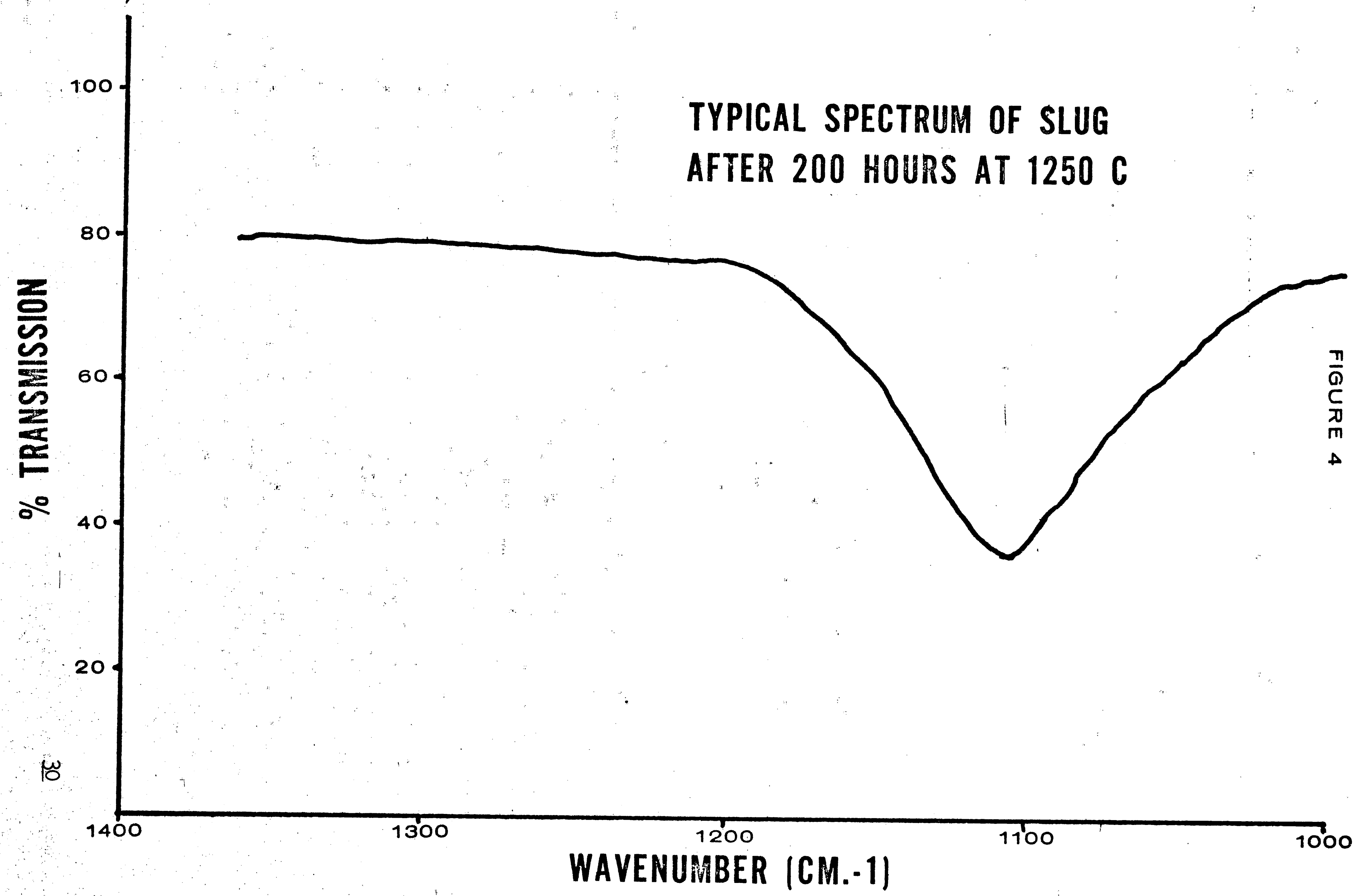


FIGURE 4

TYPICAL SPECTRUM OF 1200 ANGSTROM
SILICON DIOXIDE FILM

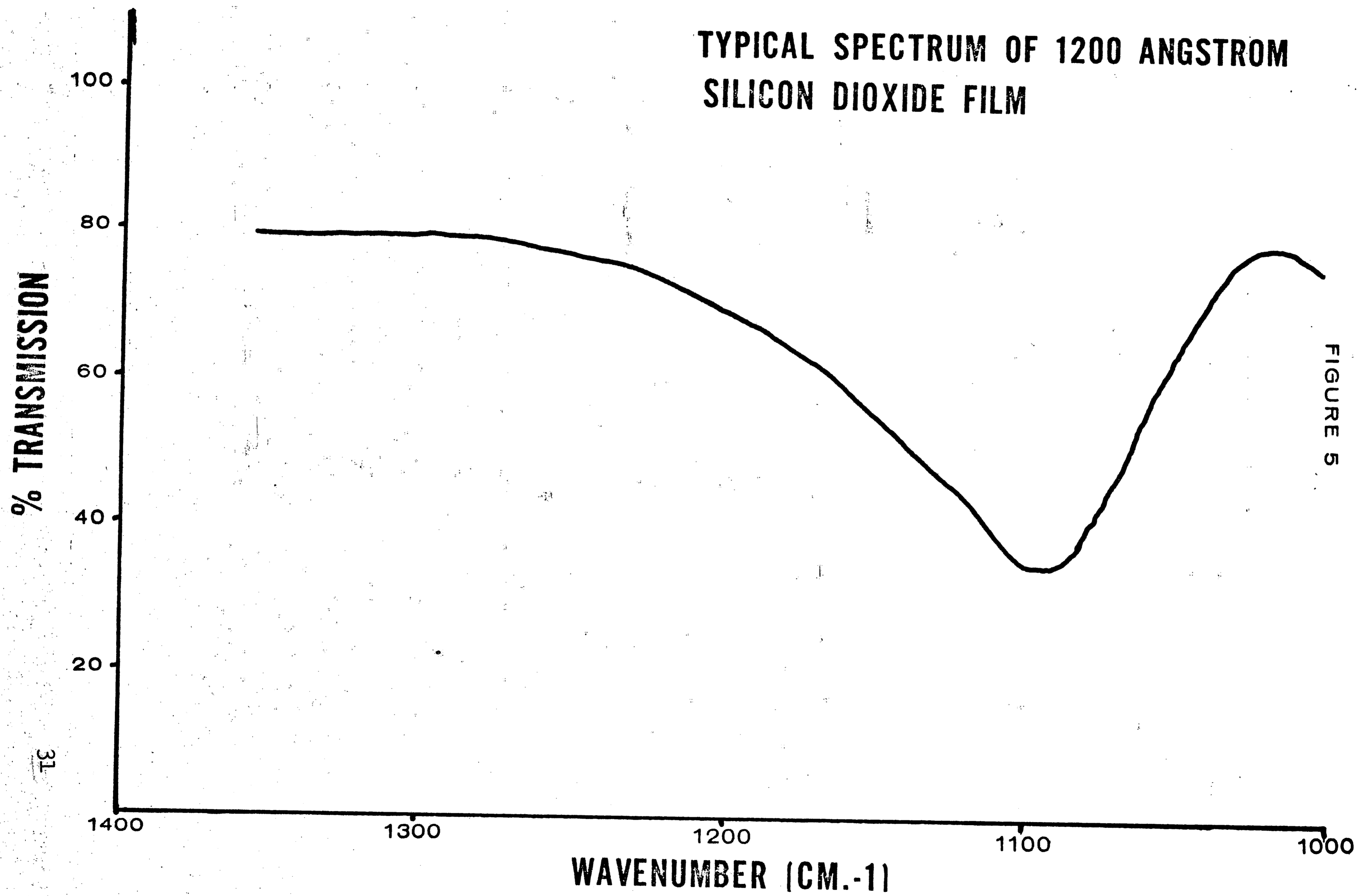


FIGURE 5

**SPECTRUM OF SLUG HEATED AT 1000 C
FROM WORK OF SMAKULA**

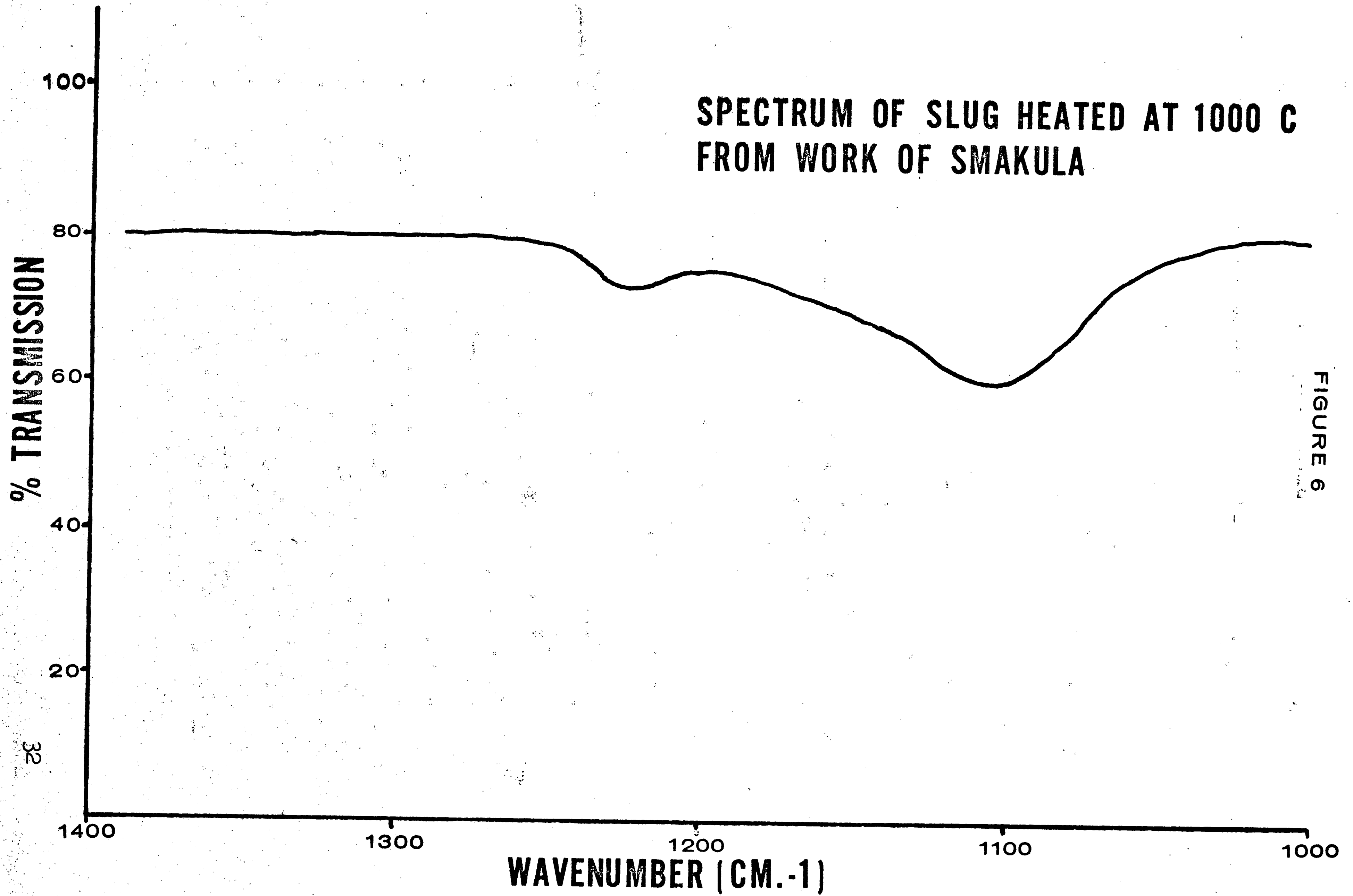


FIGURE 6

INTERSTITIAL OXYGEN CONTENT
VERSUS TIME AT 1050 C

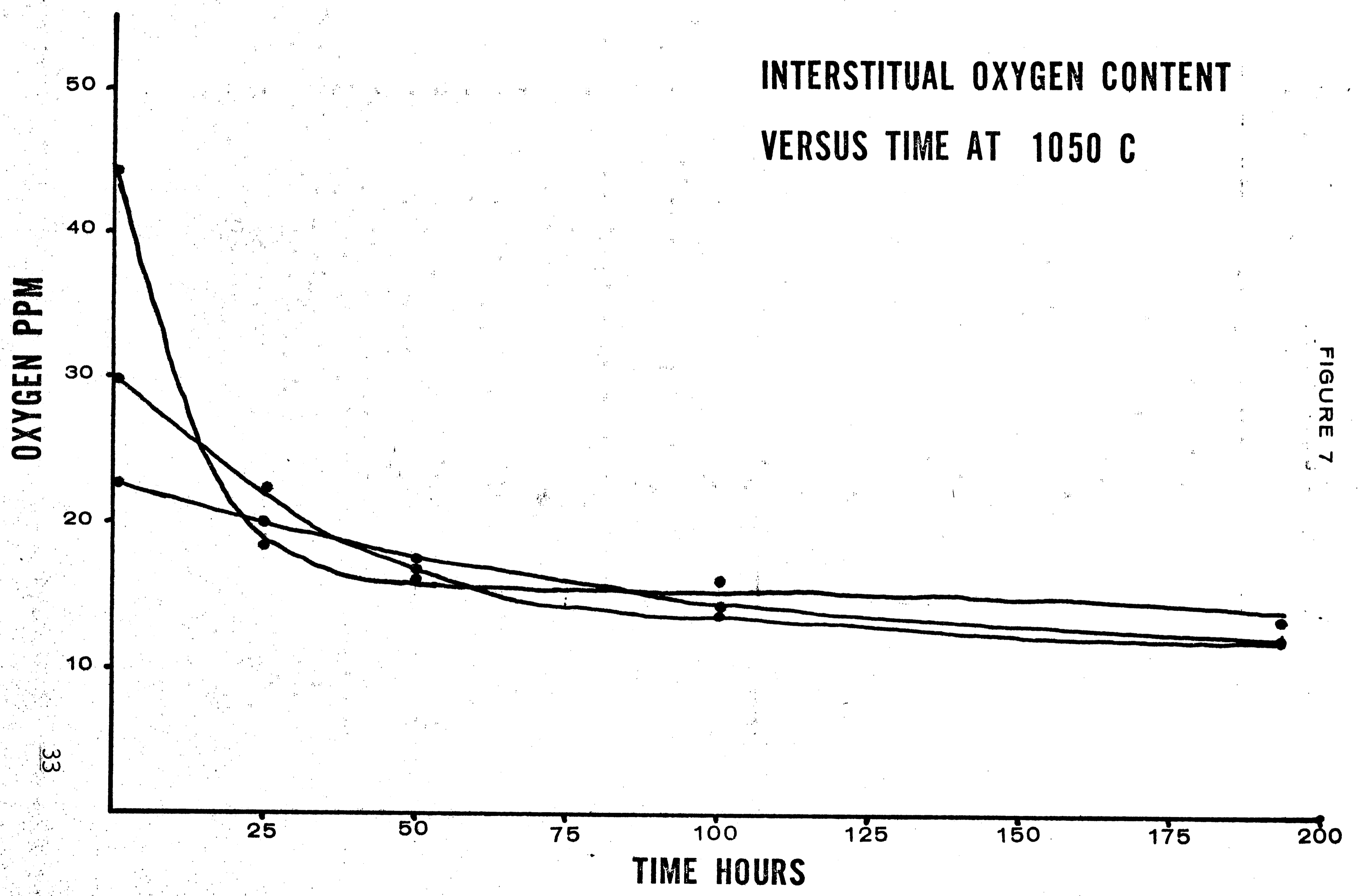


FIGURE 7

33

INTERSTITIAL OXYGEN CONTENT
VERSUS TIME AT 1250 C

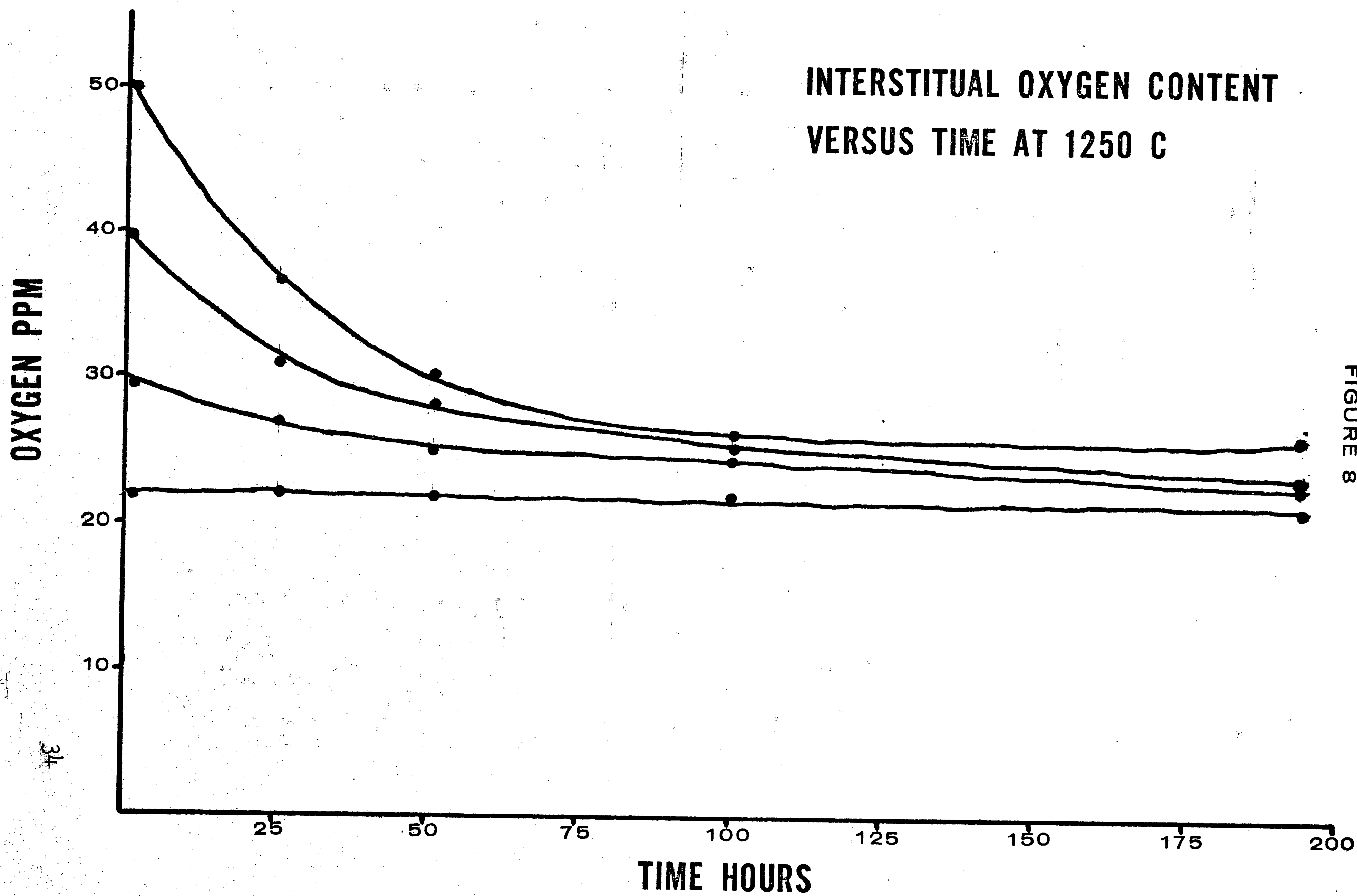


FIGURE 8