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TECHNICAL REPORT

FOR PERIOD ENDING JUNE 30, 1971

to

ADVANCED RESEARCH PROJECT AGENCY

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Title

ELECTRONIC AND RADIATION DAMAGE PROPERTIES OF RUTILE

Period:                          1 year

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            Deputy Director for Materials Sciences
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During the report period we have concentrated our effort in the following areas:

A. Crystal Growth

B. Sample Preparation

C. Devices

D. Hall Effect

E. Review Paper

F. Infrared Experiments

G. Miscellaneous

## A. Crystal Growth

A part of the crystal growth program during the first year under this grant has involved a careful literature study of potentially useful growth techniques for rutile and the physical chemistry of certain titanium compounds which might be used as starting materials for the preparation of ultrapure $TiO_2$ in later stages. Consequently, it was decided not to employ the originally proposed chemical vapor deposition method (CVD). Rather a chemical vapor transport method (CVT) was chosen. Being carried out in a closed ampoule, CVT allows for a higher degree of controllability of growth conditions and purity. Furthermore, nucleation problems, inherent in the large change in free energy of typical CVD reactions, can be avoided with reversible transport reactions in CVT.

Since seeded (homoepitaxial) growth was planned to obtain large single crystals, the possibility of etching seeds in situ was felt to be an additional advantage of CVT over CVD. In addition to the growth of bulk crystals, vapor phase growth also allows us to produce very pure and well characterized $TiO_2$ films, (presumably epitaxial, on suitable substrates) which will be important for device applications.

The following consecutive goals were set and detailed plans were worked out for their realization:

1. Systematic study of the optimum growth conditions for large single crystals of rutile with high structural quality -- without specific concern for purity.

2. Preparation of ultrapure $TiO_2$ powder as starting material for ultrapure single crystals.

3. Development of techniques to dope ultrapure $TiO_2$ controlled during growth from the vapor phase.

Good progress has been achieved already towards goal 1. Since commercial equipment does not allow for optimization of the temperature profile required in CVT, a novel two-zone furnace was developed which also permits direct visual monitoring of the growth process -- a feature which has proven invaluable as a time saver. The runs performed so far have already resulted in the growth of single crystals of dimensions 12 x 12 × 1 mm within 36 hours. Laue patterns of the epitaxially grown crystals are very satisfactory. Current studies of the rate limiting parameters seem to predict that the growth rates can be even further enhanced. Optimization of the growth parameters should be realized during the next 3-4 months. A series of quantitative measurements of the growth rate as a function of various transport parameters will be a valuable contribution to the understanding of the technologically important CVT method.

Our preliminary runs have indicated some difficulty in achieving a stable growth interface, since the crystal surfaces show a marked tendency to become increasingly rough as growth proceeds, and in some cases the growth has even become dendritic in nature. The source of this difficulty is well understood; such behavior is essentially the same as is encountered in certain cases in melt growth where constitutional supercooling can occur. Elimination of this difficulty requires careful attention to the thermodynamics of the reactions, the transport mechanisms and the anisotropy of growth rate of rutile. Proper orientation of the seed and establishment of the optimum temperature profile (which will be somewhat more complicated than originally anticipated) will eliminate this problem. The work has proceeded far enough to demonstrate that our confidence in this technique is well justified.

For the realization of goal 2, the preparation of ultrapure $TiO_2$, titanium halides offer ideal properties as starting materials. In particular, $TiCl_4$ and $TiI_4$ are readily available and well suited to wet chemical purification methods as well as vacuum distillation and zone refining. In this part of the planned work we will benefit from the extensive experience of our Crystal Growth Laboratory with the ultrapurification of alkali halides,[1] a chemically very similar group of compounds. The choice of purification procedures will depend on the actual impurities in our crystals. Suitable techniques for monitoring concentration of trace impurities are being investigated.

## B. Sample Preparation

Since our Crystal Growth is not expected to produce usable crystals for a few months yet, and since the emphasis will be on very pure crystals initially, we felt it would be wise to build up an inventory of doped crystals from other sources. We now have more than 30 boules of rutile, doped with a wide variety of impurities and a considerable range of concentrations. These have all been oriented and cut. A variety of specimens for optical, dielectric loss and EPR studies have been prepared (cut to appropriate dimensions, and orientations, polished and etched where appropriate).

Considerable effort has been devoted to the problem of crystal cutting.

We had previously used a conventional diamond-impregnated cutoff wheel for this purpose. This technique leaves much to be desired, since it results in very severe surface damage, requires extensive hand-lapping of samples after cutting and is very wasteful of sample material, both because of breakage and kerf. To alleviate these problems, the Physics Department purchased a diamond-impregnated wire saw (Lastec Model No.510). Despite the fact that this is the best instrument of this type commercially available, it is rather poorly designed in several respects, and has required extensive modification. We now have the saw working nicely, however, and it has proved to be an excellent investment. For example, we estimate that the number of usable specimens which can be cut from a given boule is increased by as much as a factor of three. Since the crystals now on hand cost in excess of $2,000, and preparation time has been greatly reduced, the savings is obviously substantial.

Some additional effort has also been devoted to the problem of developing suitable etching techniques. Previous dielectric loss studies had demonstrated the importance of eliminating all surface damage before attempting to make electronic measurements, and etching procedures adequate for bulk dielectric loss studies had already been developed. However, fabrication of the electronic devices described in our original proposal requires not only that the surfaces be free of damage, but also that they be smooth, to eliminate the possibility of variation in thickness and pin-hole effects in the materials to be deposited on the surface. Hence, we have made a more detailed investigation of the etching process, utilizing both the scanning electron microscope and interference contrast optical microscopes. It was found that adequate pre-preparation of the crystal surfaces and minor modification of the KOH etching procedure yields quite satisfactory surfaces. This program also involved development of less severe mechanical polishing techniques than are normally used (i.e., a high-

speed teflon lap of our own design, coupled with a "soft" abrasive). These problems now appear to have been solved.

## C. Devices

During the report period our work on devices has centered mainly on producing sufficiently smooth, damage-free surfaces as discussed in Section B.

The next phase in the production of MOS-type devices is the application of $SiO_2$ insulating layers. As mentioned in earlier reports, arrangements have been made for doing this, and the simplest configurations should be available for testing shortly.

The production of junction devices, of course, requires P-type rutile. Recent experiments with Schottky barrier devices for a few dopants have suggested a weak P-type conductivity. The Hall Effect measurements discussed in Section D will answer this question. These measurements and experiments with other promising dopants are a necessary prelude to junction device work.

## D. Hall Effect

The value of Hall Effect measurements has been discussed previously. Unfortunately, the low conductivity and high dielectric constant of $TiO_2$ makes the measurements very difficult. We have analyzed various methods and have concluded that the most appropriate technique for this particular crystal is to apply AC magnetic and electric fields, at different frequencies, and detect the Hall voltage at either the sum or difference frequency, using standard lock-in amplifier techniques. This approach eliminates a variety of potentially troublesome problems, such as barrier layer effects and field-induced impurity migration. The schematic is sketched below:

Signal
Gen.

Amp          Magnet

Output          Lock
In          Mixer          Filter          Amp          Sampl
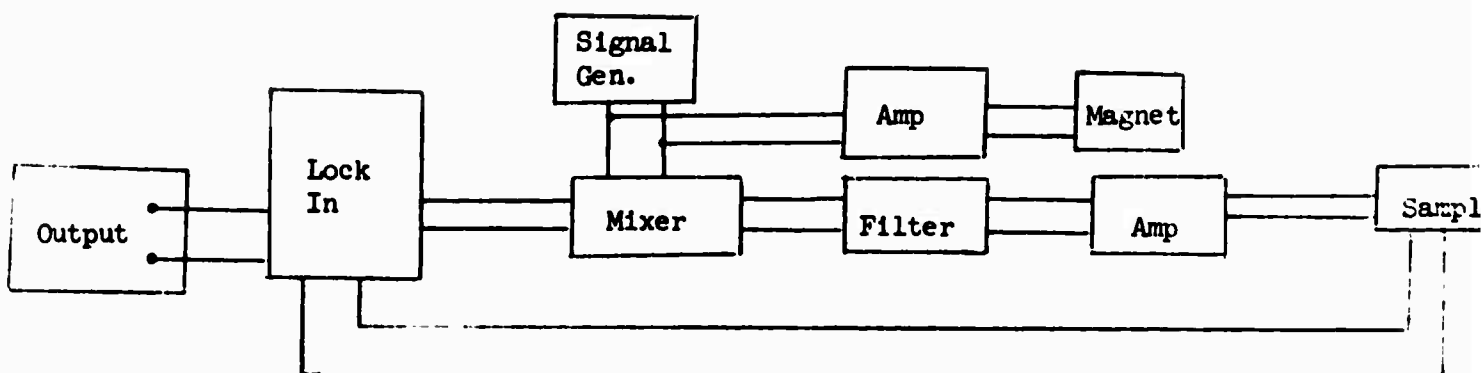
This arrangement provides great sensitivity and is reasonably simple to construct. The major experimental difficulty is the magnet. It proves to be difficult to drive an iron core magnet at sufficient frequency and field strength, although we have tested the method on Ge this way. We are presently constructing a small ferrite core magnet which will overcome this difficulty and also allow us later to extend the measurements to low temperatures as that becomes desirable.

The planned sample configuration is such that we will make Hall Effect and four terminal conductivity measurements simultaneously.

Room temperature results on samples with various doping are expected shortly. We will then extend the experiments to low temperatures where appropriate

### E.  Review Paper

The review paper on rutile is progressing well. The sections on the thermal properties and the phonon spectrum are completed; the sections on optical properties, mechanical properties, electronic band structure, and electrical properties are almost completed.

Presently, besides finishing the above sections, we are starting on the magnetic properties section.

In the process of writing the review paper, several new experiments have occurred to us which will be useful in aiding our understanding of rutile. A

particularly important one, for which samples have been prepared, involves measuring the temperature dependence of an optical absorption peak at 1.5u associated with conduction electrons in rutile. This experiment is described in Sec. F.

## F. Infrared Experiments

We are studying the temperature dependence of an absorption peak at 1.5u associated with conduction electrons in rutile.

Preliminary results indicate that the strength of this absorption is proportional to the carrier concentration over several orders of magnitude. The temperature dependence of the absorption peak has been studied in only one nominally vacuum reduced sample.[2] Between $50^{\circ}K$ and $10^{\circ}K$, the 0.8ev peak disappeared and a 1.2ev peak appeared. This behavior has been interpreted as a transfer of a small polaron without lattice relaxation between bulk $Ti^{4+}$ ions for the 0.8ev peak, and polaron transfer from a defect to a neighbor $Ti^{4+}$ for the 1.2ev peak. The large frequency shift in this model arises from the frequency difference between the local and bulk lattice vibrations. If such a model is correct, then the magnitude of the frequency shift should be strongly dependent on the type of defect the electrons freeze out upon at low temperatures. In addition, the temperature at which the peak shift occurs should correlate with changes in the EPR spectrum of the defect. For example, the isoelectronic sequence $V^{5+}$, $Nb^{5+}$, and $Ta^{5+}$ are thought to enter the lattice substitutionally. EPR data indicates that these defects trap electrons at temperatures of $100\text{-}200^{\circ}K$, $28^{\circ}K$, and $10^{\circ}K$ respectively. If the "free carrier" absorption peak for samples with these dopants shows a shift at these temperatures, the change transfer model will be on excellent footing. If on the other hand there is no correlation between the EPR lines and the optical absorption, a model involving a more complicated defect structure will have to be invoked.

## G. Miscellaneous

The photoemission study has proven unnecessary due to recent work elsewhere which has measured the work function of rutile and found a value of 7.0 ± 0.5 ev.[3] This is in excellent agreement with the predictions of our model as discussed earlier.

The photoconductivity work has been set aside pending the availability of suitable crystals from our crystal growth effort.

Calculations on the band structure are proceeding, but no definite results are yet available.

# References

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2.  Bogomolov, V. N. et al., Sov. Phys. Solid State $\underline{9}$, 1630 (1968).


3.  Derbenwick, G. F., Tech Rept. No. 5220-2, Stanford Electronics Lab.