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August 12, 2004

Tim Harris
Section Chief
U.S. Nuclear Regulatory Commission
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Dear Tim,

This letter is a follow up to our conversation of 9 August 04 regarding Lake Shore Cryotronics proposal to manufacture cryogenic thermometers from neutron irradiated germanium wafers. My understanding is that since the material will be irradiated in a reactor, it is considered forever after subject to licensing if it is incorporated into a product for distribution to unlicensed individuals. Further, given the extremely low level of activity and concentration, the necessary license is one allowing us to distribute exempt concentrations of a radioactive material. Since the project involves possession, manufacturing, and distribution of an exempt concentration of material which has been irradiated in a reactor there is both an NRC and State of Ohio (an agreement state) licensing component to address. To this end, I've copied this letter to Steve James, State of Ohio Bureau of Radiation, Chief of Licensing and Inspection, (614) 728-0873 for his review.

A detailed description of the project is contained in the enclosed Detailed Project Description, A quick summary of the project is given here. Doped germanium is considered a secondary thermometer standard for cryogenic thermometry. The electrical resistivity is a strong function of temperature, and the resistivity response to temperature response can be varied with proper doping of the material. In this project, Lake Shore would provide 186 germanium wafers to the University of Missouri Research Reactor for irradiation. Note that this is a one time irradiation. No further material will be irradiated. The individual wafer physical characteristics are 5.08 cm diameter by 0.064 cm thick for a volume of 1.29 $cm^3$ and a mass of 6.85 g. These would be divided into eleven subgroups with eleven fluence (i.e. doping) levels. Neutron irradiation of the germanium wafers causes three of the five naturally occurring germanium isotopes to transmutate into gallium, arsenic, and selenium which then act as dopants for the material. The material is then referred to as NTD germanium. By varying the level of doping, i.e. the total neutron fluence, temperature response can be tailored for our targeted temperature of 4.2 K and below. After irradiation, the NTD germanium will be stored for a minimum period of one year at the University of Missouri or The Ohio State University. At that point the highest activity of a single wafer will be less than $7x10^{-9}$ Ci and will continue to decay with a half-life of 11.4 days. The remaining activity is all due to $_{32}Ge^{71}$. After 1 year, the total activity of all 186 wafers collectively will be less than 2 μCi – well below the exempt quantity limit of 100 μCi for $_{32}Ge^{71}$ established in NRC and Ohio regulations. A six-month

period of in-house testing will begin after the 1 year storage period. The wafers will then be polished, ion implanted and sawed into small sensing elements (10 mg). The sensing elements will have gold electrical leads attached and then be sealed into a 3 mm diameter × 8 mm long copper can. Electrical leads extend outside the body for user connection. At 18 months post irradiation, the earliest date that commercial sensors could be sold, the total activity of all wafers will be $2.2x10^{-11}$ Ci and the activity of a single sensing element will be $1.8x10^{-16}$ – all orders of magnitude below regulatory exempt limits. The activity concentration of wafers and sensing elements will be $9.3x10^{-8}$ μCi/ml – again orders of magnitude lower than the regulatory exempt concentration limit of $2x10^{-2}$ μCi/ml. Going beyond the 18 month period, both activity and concentration would continue to decrease by a factor of two every 11.4 days. We expect to sell fewer than 50 of these thermometers per year over the life of the product. We don't really expect to make money with this product, but we are pursing the project more as service to the low temperature scientific community because our company's position as a leader in cryogenic thermometry and the recent adoption of a temperature scale that covers the temperature region below 0.65 K (PLTS-2000).

In order to proceed with the project, I would like to have agreement between Lake Shore, the NRC, and the State of Ohio with regard to what licenses, if any, are necessary. The first and major question is whether or not the material, manufacturing, and distribution of products containing this material require licensing? At the point in time where manufacture and distribution would begin, is the quantity and concentration sufficiently low enough that it can be considered exempt? If licensing is required, what type of license(s) is required and from which agency – the NRC, the State of OH, or both?

I can think of four possible scenarios that this project can follow:

1) In this individual case, through our analysis the material activity and concentration is deemed to be so far below established regulatory exempt activity and concentration limits that it is considered to be below regulatory concern and an exemption to licensing is granted for our application. In this case, is the exemption granted by the NRC, the State of Ohio, or both?

2) There is mechanism or process whereby the irradiated material can be surveyed and, if not above background, certified to be non-radioactive releasing it from licensing. If such a mechanism or process exists, is it at the federal or state level?

3) The Ohio State University obtains the necessary license to distribute the material to Lake Shore thus releasing Lake Shore from further licensing requirements. In this case, what license amendments or additions would The Ohio State University need and from which agency?

4) Licensing is required and Lake Shore obtains the necessary licenses in order to possess, manufacture, and distribute products containing the NTD germanium. In this scenario what licenses do we need and from which agency? This scenario is complicated by the need to send the wafers out for polishing and ion implantation after the one-year storage period. While ion implanters may have licenses to possess irradiated material, it is unlikely that a polishing company would. In this scenario, we would need a mechanism whereby the material could be sent to an out-of-state polishing company that had no license to possess irradiated material.

The regulations do not really address this specific type of project. In fact, the regulations concerning manufacturing with and distribution of exempt concentrations of materials seem somewhat vague and open to interpretation depending upon the circumstances. Obviously from Lake Shore's point of view, the first two scenarios listed above are preferred as they minimize the administrative cost of the

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proposed work. An exemption to licensing would be supported by 1) this is a one-time buy with no on-going material irradiations, 2) the extremely low activity and concentration levels at the time at which manufacture would begin, and 3) the continuing decrease in activity and concentration beyond the point at which manufacturing would begin. Conversations with experts in materials irradiation at the University of Missouri Research Reactor and at The Ohio State University Nuclear Reactor Laboratory have indicated that it would be difficult to distinguish the NTD material from background at twelve months after irradiation and virtually impossible after 18 months.

I've spoken with various people at the NRC (Bruce Carrico and Bill Ward) and the State of Ohio Bureau of Radiation Protection (Mike Snee and Steve James), but no one has been able to give a definitive answer on the exact licensing needs or whether a license is necessary. Clarification on the licensing needs of the project would be greatly appreciated. My contact information is below. Thank you in advance for your help with our project.

Best regards,

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# Proposal to Fabricate Germanium Resistance Thermometers From Neutron Transmutation Doped Germanium Material

## Detailed Project Description
## Lake Shore Cryotronics, Inc.
## Dr. Scott Courts

### Project Summary

Lake Shore Cryotronics proposes to neutron irradiate germanium wafers to cause transmutation doping to occur within the wafers. These wafers would be diced into small temperature sensing elements and packaged for use as cryogenic thermometers for use in the below 4.2 K temperature range. This is considered by us to be a one-time irradiation and the material produced will last the lifetime of the product.

### Company information:

Lake Shore Cryotronics, Inc. is a small, high-technology company which specializes in cryogenic temperature sensors and instruments for control purposes. Incorporated in 1968, Lake Shore manufactures sensors and instruments capable of measuring temperature, magnetic field and other magnetic properties. The company employees about one hundred people, and roughly one third of these employees hold degrees in mechanical, electrical and nuclear engineering, as well as physics, chemistry, biology, materials science, and other technical fields. The project outlined here is an extension of the existing line of temperature sensors that we manufacture and market. Both company information and product information is also available at www.lakeshore.com.

### Purpose:

Thermometry work during the 1950s and 1960s led to the adoption of germanium resistance thermometers (GRTs) as secondary thermometer standards for cryogenic temperatures by national laboratories. Their use was instrumental in the development of the International Provisional Temperature Scale of 1976. The resistivity of a doped germanium element is a strong function of temperature. A typical GRT may increase from 10 Ω at 100 K to 100,000 Ω at 1 K. At lower temperatures, GRTs have an extremely high sensitivity and are stable to better than 0.001 K over repeated thermal cycling making them ideal for a temperature sensor. As a result of their high sensitivity, however, their resistance exponentially increases beyond practically measurable values thus limiting the useful range of a single germanium thermometer. This limitation is addressed by fabricating devices from material with various levels of doping

creating a family of devices that cover the necessary temperature ranges. In this manner, a single device may cover the 0.05 K to 1 K range, the 0.5 K to 20 K range, or the 1.4 K to 100 K range.

Doping of the germanium material is accomplished in one of two ways. The first method, the Czochralski (CZ) method, involves melting bulk germanium metal, introducing the required dopants, and finally allowing the melt to freeze as a single crystal. This method is very difficult to control and large doping gradients result. The final material is nonuniform and yields from sensing elements cut from this material are low, especially for sensors whose target temperature range is below 4.2 K. A second method of doping the germanium is accomplished through neutron transmutation doping (NTD) whereby germanium wafers are irradiated by neutrons. This causes three of the naturally occurring germanium isotopes to transmutate into desirable dopants in a well defined manner. Germanium material produced in this manner is very uniform with predictable behavior for sensors targeted for use below 4.2 K. While the process is well understood, both p-type and n-type dopants are created which work against one another and limit devices fabricated via this method to use at temperatures below 4.2 K.

## The NTD Germanium Process

This following procedure is outlined by N. P. Palaio in his Masters Thesis, "Development of Neutron-Transmutation-Doped Germanium Bolometer Material," Lawrence Berkeley Laboratory, University of California, Materials and Molecular Research Division, 1983.

Five germanium isotopes occur naturally in commercially available germanium wafers. The isotopes and their relative abundance are listed in Table 1.

TABLE 1. Germanium isotopes and relative abundance in unirradiated wafers.

| Isotope | % of material |
|---|---|
| $_{32}Ge^{70}$ | 20.5 |
| $_{32}Ge^{72}$ | 27.4 |
| $_{32}Ge^{73}$ | 7.8 |
| $_{32}Ge^{74}$ | 36.5 |
| $_{32}Ge^{76}$ | 7.8 |

The reactions that occur due to neutron irradiation of the germanium wafers are listed in Table 2.

TABLE 2. Expected transmutations, cross sections and half-lives for neutron transmutation doped germanium wafers. Cross sections and Half-life data are from F. William Walker, Josef R. Parrington and Frank Feiner's "Nuclides and Isotopes," Fourteenth Edition, General Electric (San Jose, CA) 1989.

| Isotope Fraction | Reaction | Cross Section (barns) | Half-life |
|---|---|---|---|
| 20.5 | $_{32}Ge^{70}$ (n,γ) $_{32}Ge^{71}$ → $_{31}Ga^{71}$+K | 3.25 | 11.4 days |
| 27.4 | $_{32}Ge^{72}$ (n,γ) $_{32}Ge^{73}$ | 1.00 | Stable |
| 7.8 | $_{32}Ge^{73}$ (n,γ) $_{32}Ge^{74}$ | 15.0 | Stable |
| 36.5 | $_{32}Ge^{74}$ (n,γ) $_{32}Ge^{75}$ → $_{33}As^{75}$ + β$^-$ | 0.52 | 82.8 minutes |
| 7.8 | $_{32}Ge^{76}$ (n,γ) $_{32}Ge^{77}$ → $_{33}As^{77}$ + β$^-$<br>→ $_{34}Se^{77}$ + β$^-$ | 0.16 | 11.3 hours<br>38.8 hours |

For the reactions listed, the number of atoms transmuted by each reaction is given by

$$N_{Transmuted} = N_{total} \text{ x (\% of total atoms producing transmuted atoms) x (reaction cross section x (fluence)} \quad (1)$$

Given a germanium wafer, the number of reactant atoms of each isotope is fixed by the physical size of the wafer. In addition, the reaction cross sections (experimentally determined) are fixed for each of the reactions. This forces the number of resulting gallium, arsenic and selenium atoms to form in a constant ratio given by

$$Ratio = \frac{N_{As} + 2N_{Se}}{N_{Ga}} = 0.322 \quad (2)$$

where $N_{Ga}$, $N_{As}$ and $N_{Se}$ are the number of gallium, arsenic and selenium donors respectively. The factor of 2 for selenium is due to the fact that it is a double donor. This can also be stated by saying that of all donors, 75.62% will be gallium donors, 21.55% will be arsenic donors and 2.83% will be selenium donors. This ratio is related to the number of net donors in the NTD germanium and is computed in this manner because arsenic and selenium are n-type dopants while gallium is a p-type dopant. The NTD germanium material is p-doped overall.

## Specific to Lake Shore Cryotronics' Project

Our project targets germanium resistance thermometers for the temperature range below 4.2 K. While the irradiation process is well understood, quantifying the neutron flux/fluence for

the irradiation process introduces some uncertainty probably on the order of 10% to 15%. To compensate, multiple target total fluences are included in our project. For our project, 186 germanium wafers have been divided into eleven groups and each group will be irradiated to one of eleven target fluences ranging from $2.77 \times 10^{18}$ n/cm$^2$ to $2.39 \times 10^{19}$ n/cm$^2$. The highest fluence, hence the highest activity, is used for the calculations in the rest of this section.

Each germanium wafer is approximately 5.08 cm diameter x 0.0635 cm thick for a volume of 1.29 cm$^3$. Using an average density of 5.32 g/cm$^3$ for germanium, the approximate mass is 6.85 grams per wafer. The thermometer sensing elements cut from this wafer will be approximately 0.063 cm x 0.102 cm x 0.305 cm in size with a mass of 10.5 milligrams per sensing element. We expect sales for sensors in the targeted temperature range to be on the order of 50 sensors per year. A single wafer could supply over 500 temperature sensors which would be a ten year supply.

The initial germanium material is expected to consist of the germanium isotopes of relative abundance listed in Table 1. In addition to the germanium isotopes, the expected major impurities for this grade germanium, their impurity level, expected reactions, reaction cross sections and half-lives are given in Table 3. This information was provided by Angela Oliver, Engineer at Eagle-Picher Industries.

TABLE 3. Expected impurity isotopes, impurity level, reactions, reaction cross sections and half-lives for neutron transmutation doped germanium wafers. Cross sections and Half-life data are from F. William Walker, Josef R. Parrington and Frank Feiner's "Nuclides and Isotopes," Fourteenth Edition, General Electric (San Jose, CA) 1989.

| Isotope | ppm | Reaction | Cross Section (barns) | Half-life |
|---|---|---|---|---|
| $_{14}Si^{28}$ | 0.3 | $_{14}Si^{28}$ (n,γ) $_{14}Si^{29}$ | 0.257 | Stable |
| $_{12}Mg^{24}$ | 0.3 | $_{12}Mg^{24}$ (n,γ) $_{12}Mg^{25}$ | 0.085 | Stable |
| $_{11}Na^{23}$ | 0.2 | $_{11}Na^{23}$ (n,γ) $_{11}Na^{24} \rightarrow {}_{12}Mg^{24} + \beta^-$ | 0.53 | 14.96 hours |
| $_{16}S^{32}$ | 0.1 | $_{16}S^{32}$ (n,γ) $_{16}S^{33}$ | 0.79 | Stable |
| $_{19}K^{39}$ | 0.1 | $_{19}K^{39}$ (n,γ) $_{19}K^{40}$ | 3.1 | Stable |

Using an averaged gram atomic weight of 72.59 grams for germanium, a single wafer would contain about

(6.85 grams/72.59 grams)xAvogadro's number = $5.68 \times 10^{22}$ atoms.

After neutron irradiation, the resulting number of transmuted atoms can be calculated for each isotope using Equation 1. Based on wafers irradiated for Lake Shore by the University of Missouri Research Reactor in 1986, the highest gallium donor concentration needed (taking into account the reactor uncertainties) is roughly $7x10^{17}$ gallium atoms/$cm^3$. This requires

($7x10^{17}$ gallium atoms/$cm^3$)x(1.29 cm3/wafer) = $9.03x10^{17}$ gallium atoms/wafer.

Rearranging Equation 1 and solving for the maximum fluence yields

Fluence = $N_{Transmuted}$ / (Reaction Cross Section x Number of reaction atoms)

= ( $9.03x10^{17}$ Ga atoms) / ( $3.25x10^{-24}$ $cm^2$ x $5.68x10^{22}$ atoms x 0.205 )

Fluence = $2.39x10^{19}$ n/$cm^2$.

Using this maximum fluence, the number of transmuted atoms in each reaction can be calculated. During this process, radioactive byproducts are formed which decay into the desired dopants. The activity level for each isotope can next be calculated by

$$\lambda = \frac{\ln 2}{t_{1/2}}$$

where $t_{1/2}$ is the half-life. The initial activity, $A_0$, is calculated using the number of atoms of each particular isotope immediately after irradiation, i.e. $A_0 = dN/dt = -\lambda N$. The activity then decays exponentially according to

$$A(t) = A_0 e^{-\lambda t}$$

where t is the time. Activity in decays per unit time can be converted into units of curies using the relation 1 curie = $3.7x10^{10}$ decays/second. Table 4 lists the expected activities for each isotope at various points in time.

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TABLE 4. Expected activities as a function of time after irradiation.

| Isotope | Half-life | Activity (curies) at elapsed time | | | | |
|---|---|---|---|---|---|---|
| | | Initial | 1 Month | 2 Months | 4 Months | 6 Months |
| $_{32}Ge^{71}$ | 11.2 day | 22.0 | 3.56 | 0.574 | 0.0149 | $3.9x10^{-4}$ |
| $_{32}Ge^{75}$ | 82.2 min. | 1244.3 | 0 | 0 | 0 | 0 |
| $_{32}Ge^{77}$ | 11.3 hr. | 9.99 | $6.6x10^{-19}$ | 0 | 0 | 0 |
| $_{33}As^{77}$ | 38.8 hr. | 0.61 | $2.0x10^{-6}$ | $6.6x10^{-12}$ | 0 | 0 |
| $_{11}Na^{23}$ | 14.96 hr | $6.4x10^{-5}$ | $2.1x10^{-19}$ | 0 | 0 | 0 |
| TOTAL ACTIVITY: | | 1276 | 3.56 | 0.574 | 0.0149 | $3.9x10^{-4}$ |

| Isotope | Half-life | Activity (curies) at elapsed time | | | | |
|---|---|---|---|---|---|---|
| | | 8 Months | 10 Months | 12 Months | 18 Months | 24 Months |
| $_{32}Ge^{71}$ | 11.2 day | $1.0x10^{-5}$ | $2.6x10^{-7}$ | $6.9x10^{-9}$ | $1.2x10^{-13}$ | $2.1x10^{-18}$ |
| $_{32}Ge^{75}$ | 82.2 min. | 0 | 0 | 0 | 0 | 0 |
| $_{32}Ge^{77}$ | 11.3 hr. | 0 | 0 | 0 | 0 | 0 |
| $_{33}As^{77}$ | 38.8 hr. | 0 | 0 | 0 | 0 | 0 |
| $_{11}Na^{23}$ | 14.96 hr | 0 | 0 | 0 | 0 | 0 |
| TOTAL ACTIVITY: | | $1.0x10^{-5}$ | $2.6x10^{-7}$ | $6.9x10^{-9}$ | $1.2x10^{-13}$ | $2.1x10^{-18}$ |

Table 4 shows that by about one month after irradiation the activity of the $_{32}Ge^{71}$ clearly dominates the activity of the each wafer. The decay mode for $_{32}Ge^{71}$ is via electron capture to $_{31}Ga^{71}$ with a decay energy of 0.229 MeV. (Note: Values for the activity of $_{33}As^{77}$ are based on the unrealistic assumption that all of the $_{32}Ge^{77}$ decays immediately after the irradiation process ceases. This does not occur, but at the 6 month mark, it doesn't matter.) Activity levels below $10^{-20}$ curies are listed as 0 curies in Table 4.

In terms of concentration of radioactive material, after Month 4 of storage, all of the activity is due to the presence of $_{32}Ge^{71}$. The activity and concentration of the $_{32}Ge^{71}$ material as a function of time is given in Table 5.

TABLE 5. Expected activity and concentration of $_{32}Ge^{7}$ as a function of time after irradiation.

| Isotope $_{32}Ge^{71}$ | Activity (Ci) and Concentration (μCi/mL) at time after irradiation | | | | | | |
|---|---|---|---|---|---|---|---|
| | 4 months | 6 months | 8 months | 10 months | 12 months | 18 months | 24 months |
| Activity (Ci) | 0.0149 | $3.9x10^{-4}$ | $1.0x10^{-5}$ | $2.6x10^{-7}$ | $6.9x10^{-9}$ | $1.2x10^{-13}$ | $2.1x10^{-18}$ |
| Concentration (μCi/mL) | 11,550 | 302.3 | 7.75 | 0.21 | $5.4x10^{-3}$ | $9.3x10^{-8}$ | $1.6x10^{-12}$ |

The University of Missouri, the facility performing the irradiation, will store the wafers twelve months before release or ship them to The Ohio State University for storage before release. At the one-year mark, the activity per wafer will be less than $7x10^{-9}$ Ci (7 nCi). This activity will be due entirely to the $_{32}Ge^{71}$ and the activity will continue to decay with a half-life of about 11.4 days or roughly a decade decrease every 38 days. All other transmutated products will have activities well below $10^{-20}$ Ci by the end of the fourth month. Once again, this analysis has been completed for the germanium wafers that will have the highest level of activity.

After one year of storage, the activity of each wafer will be $7x10^{-9}$ Ci, and the sum total activity of all wafers will be less than 1.3 μCi – well below the exempt quantity limit of 100 μCi for $_{32}Ge^{71}$ established by federal (CFR 10, Part 30.70 Schedule A) and Ohio state regulations (Ohio Administrative Code 3701-40-8 Appendix). Additionally, the concentration of $_{32}Ge^{71}$ for each wafer will be less than 0.0054 μCi/ml – much less than the exempt concentration limit of 0.0200 μCi/ml established by federal (CFR 10, Part 30.71 Schedule B) and Ohio state regulations (Ohio Administrative Code 3701-40-11 Appendix).

At the end of the one-year storage period, the wafers will be polished to remove surface defects and ion implanted to allow gold wire bonding to the material. The wafers will then be diced and sample thermometers from wafers at each doping level (i.e. fluence level) fabricated and tested. These tests include measuring dopant concentrations, measuring the resistance as a function of temperature, and measuring stability of the fabricated devices. A minimum of six months is allotted for this testing.

We expect that the first reasonable distribution date for a commercial sensor would be at least 18 months wafer irradiation. At that point in time, the maximum activity for an individual wafers would be $1.2x10^{-13}$ Ci and the maximum activity for an individual sensing element would be $1.8x10^{-16}$ Ci compared to the regulatory limit of 100 μCi. The maximum concentration at 18 months post irradiation would be $9.3x10^{-8}$ μCi/ml compared to the regulatory exempt concentration limit of $2x10^{-2}$ μCi/ml. Both activity and concentration continue to decrease by a factor of two every 11.4 days (i.e. the half-life of $_{32}Ge^{71}$). Additionally, the sensors are mounted and epoxy sealed inside a 3 mm diameter by 8 mm long gold-plated copper can. Customers using these sensors will have no direct contact with the element. A schematic of this package is shown

in Figure 1. This is a standard package that Lake Shore has used for thirty years to package Czochralski method doped germanium resistance temperature sensors and it would be used for the NTD germanium material produced in this project.

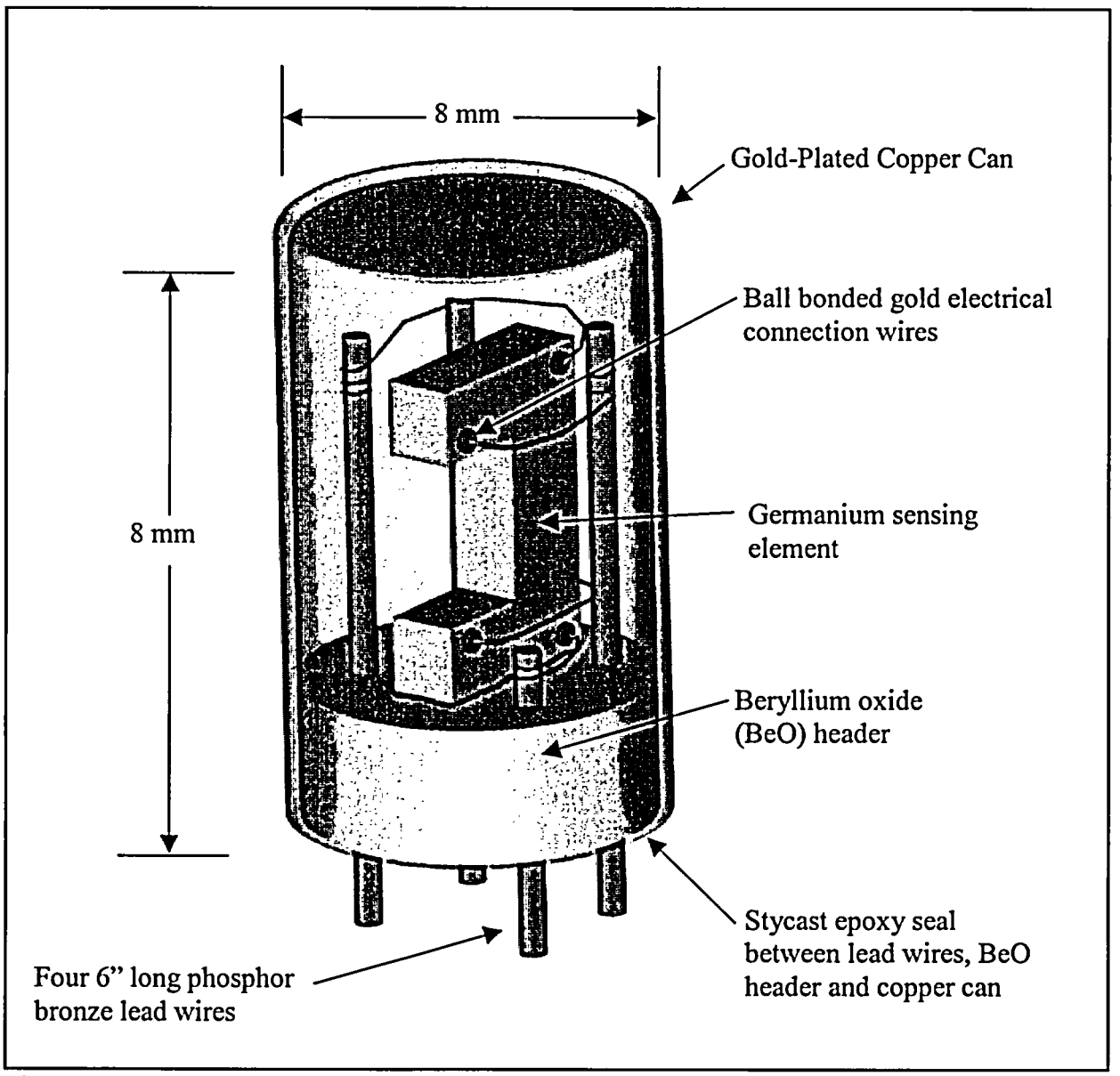


Figure 1. Standard packaging for a germanium resistance temperature sensor to be fabricated from material produced in this proposal.