# HIGH TEMPERATURE NANOSCALE MECHANICAL PROPERTY MEASUREMENTS

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*A depth sensing indentation instrument widely used for measuring the small scale mechanical properties of thin films and surfaces has been modified for operation at elevated temperatures. The essential feature permitting this development is the vertical orientation of the specimen, which allows the heated zone to be placed above the high sensitivity displacement transducer. In the present work, small scale hardness and elastic modulus measurements were performed on glass, gold, and single crystal silicon at room temperature and 200°C. The results show that at 200°C the hardness and elastic modulus of soda lime glass and gold are lower than at room temperature, as anticipated. In contrast, indentation testing of Si(100) at 200°C produced a similar hardness value to that obtained at room temperature, although the modulus was again reduced, from 140·3 to 66·0 GPa. In addition, the well known 'pop out' event, which is observed during unloading of a silicon indentation at room temperature, disappeared at 200°C.*

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## INTRODUCTION

Over the past 20 years, the depth sensing indentation technique for small scale mechanical property measurement has reached a mature stage of development and has found many applications, particularly in the field of surface engineering.[1-3] However, most of the measurements carried out so far have been limited to room temperature, since instruments for slow measurement of nanoscale displacements are generally highly sensitive to thermal expansion.

Clearly, measurement of the mechanical properties of surface engineered materials at elevated temperatures would open up significant new possibilities for the materials scientist. For example, wear resistant coatings and surfaces generally experience temperatures significantly above room temperature during normal service, and it is well known that both the hardness and modulus of such materials can be strongly dependent on temperature. As an illustration, the Young's modulus data for aluminium and tungsten shown in Table 1 were taken from the literature.[4] From Table 1 it can be seen that increasing the temperature of aluminium by 500 K, for example, leads to a drop of almost 30% in modulus, compared with a drop of about 12% in the tungsten modulus on raising its temperature by around 1200 K.

For wear resistant coatings, performance is strongly influenced by the relationship between the film and substrate mechanical properties. It is clearly desirable to determine these properties at the service temperature rather than to extrapolate the results of room temperature measurements. In addition, many microelectronic thin film structures are produced and processed at temperatures of several hundred degrees, and a complete understanding of the interactions between the materials used can be obtained only by taking measurements across the full temperature range rather than only at room temperature.

There are numerous further applications to justify elevated temperature measurements, including indentation creep studies, scratch testing of polymer coatings and other thin films, and the investigation of temperature sensitive fibre–matrix bonding forces.

## EXPERIMENTAL CONFIGURATION

Instruments for routinely measuring the mechanical properties of materials on a very small scale have hitherto been limited to room temperature operation. One factor responsible for this is that in most nanoscale instruments the displacement transducer is placed above the specimen, thus leading to unacceptably high thermal drift at higher temperatures. In the present work, a novel transducer arrangement has been used which obviates this problem.

The NanoTest 600 instrument manufactured by Micro Materials Ltd has been modified to permit high temperature operation. The principle of the NanoTest is shown in Fig. 1, from which it can be seen that the specimen is mounted vertically, opposite the displacement transducer. In indentation mode, a current in the coil causes the pendulum to rotate on its frictionless pivot so that the diamond penetrates the specimen surface. Displacement of the diamond is measured by means of the parallel plate capacitor shown. The modified NanoTest instrument is depicted in Fig. 2. This has several important new features, as follows.

First, the capacitor has been moved from its original position with a strong thermal connection to the metallic diamond holder to the bottom of the pendulum. This is possible because the bottom of the pendulum is outside the indentation force loop, that is it does not undergo elastic deformation during indentation.

Second, a copper thermal shield has been interposed between the pendulum and the hot stage to preclude any significant radiant heating of the pendulum. Heat sink fins are mounted at the top of the shield. The diamond holder passes through a small hole in the copper plate in such a way that the close proximity of the two surfaces limits heating of the diamond holder.

Third, a tiny heater capable of maintaining a temperature of 500°C and a miniature thermocouple have been added to the diamond stub, close to the tip itself. With both the diamond and specimen at the same temperature, heat flow between them does not

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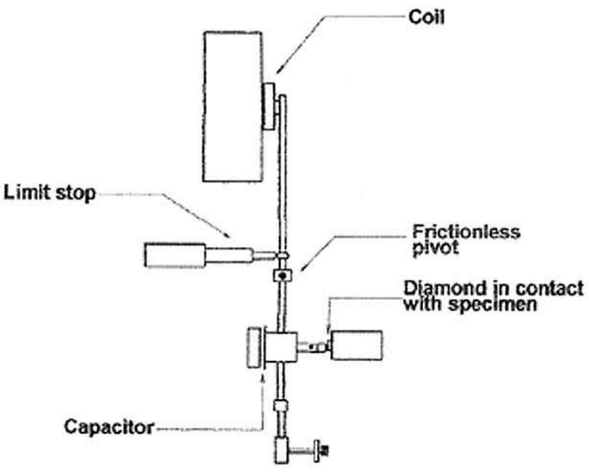


1 *Schematic diagram of NanoTest 600 pendulum configuration before modification*

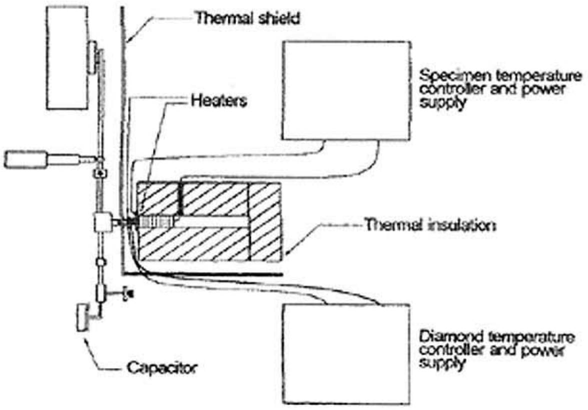
occur upon contact, thus preventing instantaneous dimensional changes resulting from thermal expansion.

Fourth, the hot stage itself consists of a thermally insulating ceramic block which is attached to the specimen holder plate normally used. With the heater at 500°C, the increase in temperature of this plate is typically less than 1°C. The wire wound heater is attached only at the outer end so that expansion occurs into the ceramic block. The control thermocouple is mounted on the outer surface of the specimen holder adjacent to the specimens themselves. Proportional temperature controllers with automatic tuning are used for both the main hot stage and the diamond heater.

Finally, any diamonds or other test probes must be fabricated such that the operating temperature will have no deleterious effect (in the present study brazing was used for the indenter instead of the more common adhesive bonding) and for reactive specimens the environmental cabinet must be purged with an inert gas.

**Table 1 Young's modulus *E v.* temperature data for aluminium and tungsten: data taken from Ref. 4 and produced using standard techniques**

| | *E*, GPa | |
|---|---|---|
| Temp., K | Al | W |
| 300 | 70·3 | 409·6 |
| 350 | 68·9 | ... |
| 373 | ... | 406·8 |
| 400 | 67·0 | ... |
| 450 | 65·0 | ... |
| 473 | ... | 403·0 |
| 500 | 62·9 | ... |
| 550 | 60·9 | ... |
| 573 | ... | 399·1 |
| 600 | 58·8 | ... |
| 650 | 56·7 | ... |
| 673 | ... | 395·1 |
| 700 | 54·6 | ... |
| 750 | 52·4 | ... |
| 773 | ... | 391·0 |
| 800 | 50·2 | ... |
| 873 | ... | 386·7 |
| 973 | ... | 382·3 |
| 1073 | ... | 377·7 |
| 1273 | ... | 368·2 |
| 1473 | ... | 358·2 |



2 *Schematic diagram of high temperature NanoTest configuration, showing both diamond and specimen heaters*

## EXPERIMENTAL PROCEDURE

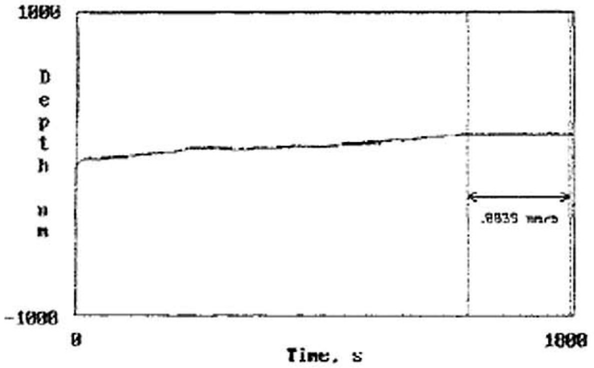
The modified NanoTest was placed in an environmental enclosure which was about 2°C above room temperature. The enclosure was temperature controlled to within better than 0·1°C. This is normal practice and is intended simply to prevent any influence from changes in room temperature.

Three specimens were selected for investigation, and these were mounted on the same stub by means of a magnesium silicate ceramic cement. The three specimens consisted of mechanically polished pure gold, soda lime glass, and (001) single crystal silicon. Indentations were performed on the three specimens at both room temperature and 200°C. The following indentation parameters were used for all measurements: 50 mN maximum load, 2·38 mN $s^{-1}$ loading rate, 10 s dwell time at maximum load.

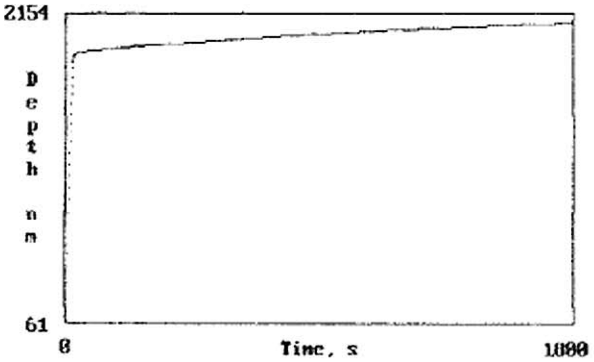
For averaging purposes, three indentations were performed for each room temperature experiment and 10 were performed for each 200°C experiment. The following experimental procedure was adopted: starting from room temperature, the specimen temperature and diamond temperature were set to 200°C and the system was left for 3 h (typically) to achieve thermal equilibrium; a depth calibration was performed at the operating temperature to preclude any errors arising from possible small changes in equilibrium capacitor spacing at the new temperature; before each test, the specimen was held within a few nanometres of the diamond for 5 min using specially written software; indentation or creep testing was performed in the normal manner. The indentation procedure was fully automated so that, for example, at 200°C 10 indentations would be performed sequentially in a line with a hovering step immediately before each one.

## RESULTS

By performing low load creep measurements without significant indentation occurring, it has been demonstrated that thermal drift in the NanoTest can be negligible even at elevated temperatures. Figure 3 shows a 200°C thermal drift measurement performed without the use of a diamond heater, although the diamond was held at a distance of approximately 0·5 μm from the specimen surface for 15 min before making contact. A constant load of 0·5 mN was used and the specimen was a Cu–Ni alloy. Clearly, even



3 *Thermal drift data for Cu–Ni alloy specimen at 200°C without use of diamond heater: ultimate drift value is only 0·0039 nm s$^{-1}$*

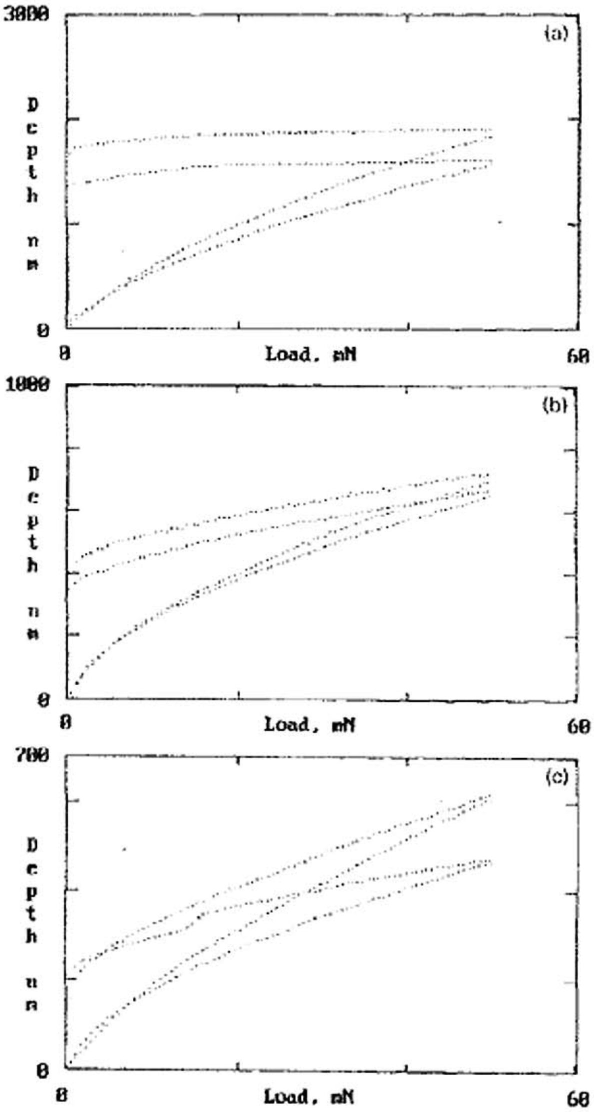


4 *Averaged indentation creep data for pure gold at 200°C under 50 mN load*

in this case the thermal drift during the short periods necessary for indentation was generally acceptable, and the ultimate value towards the end of the experiment was only 0·0039 nm s$^{-1}$.

Indentation creep occurs at room temperature even in high melting point metals such as tungsten. For investigation of this phenomenon, it is obviously of paramount importance to eliminate any significant thermal drift. The use of a diamond heater facilitates creep measurement by eliminating heat transfer on specimen–diamond contact. In fact without a diamond heater, heat transfer actually increases during the indentation owing to the increasing contact area.

The data presented in Fig. 4 were obtained at 200°C using a Berkovich indenter, a gold specimen, and an abruptly applied load of 50 mN. As mentioned above, before the load application, the diamond hovered just above the specimen for 5 min. After the initial rapid depth increase, the plot has the form of a conventional creep curve for a bulk material and can be used to calculate stress exponents. Work in this particular area, however, is still at an early stage. Obviously, for soft or low melting point materials it may be advisable to perform creep measurements at the outset of indentation testing in order to clarify the significance of time dependent effects.



*a* gold; *b* glass; *c* silicon

5 *Room temperature and 200°C indentation curves for given specimens: upper curves obtained at 200°C*

The averaged indentation results for gold are shown in Fig. 5*a*. Qualitatively the curves have similar forms, exhibiting very little elastic recovery, as would be expected for this material. It is clear from the penetration depths read from the curves that significant softening occurred during heating. Some of this was undoubtedly a result of annealing of the work hardened layer caused by mechanical polishing. This would have occurred during the initial 3 h 'warming up' period after the heaters were first switched on at room temperature. Indentation results for glass are shown in Fig. 5*b*. Again it is clear that softening occurred on heating, and also that more creep took place at 200°C during the 10 s dwell period at maximum load.

Hardness and reduced modulus values for gold and glass are presented in Table 2. As can be seen, reductions in both parameters occurred on heating.

**Table 2 Hardness *H* and reduced modulus $E_r$ values for soda lime glass, gold, and (001) single crystal silicon at room temperature and 200°C**

| | *H*, GPa | | $E_r$, GPa | |
|---|---|---|---|---|
| Material | Room temp. | 200°C | Room temp. | 200°C |
| Glass | 7·09 ± 0·09 | 5·70 ± 0·06 | 75·1 ± 0·5 | 70·6 ± 1·8 |
| Gold | 0·85 ± 0·01 | 0·59 ± 0·02 | 95·5 ± 2·7 | 80·2 ± 8·6 |
| Silicon | 12·87 ± 0·15 | 11·58 ± 0·49 | 140·3 ± 1·8 | 66·0 ± 1·6 |

The room temperature reduced modulus value for gold was 95·5 GPa, as opposed to a literature reduced modulus value of 98 GPa. At 200°C, this fell to 80·2 GPa, which is a larger decrease than anticipated. An important factor here is the relationship between the work hardened and annealed surfaces; the former would tend to exhibit pile-up, whereas the latter would exhibit sinking in, thus affecting the relative contact areas to a greater or lesser extent.

Room temperature and 200°C indentation curves for silicon are shown in Fig. 5*c*. As can be seen, these curves are significantly different from those for gold and glass. The room temperature curve shows the well known abrupt change in slope during unloading. There are several opinions as to the origin of this effect. Pharr, for instance, suggests that it is caused by a transition from a diamond structure to a b tin structure at a pressure of 10–12 GPa, with a corresponding volume reduction of about 20%, the development of a compressive stress state during unloading because of the volume difference, and the formation of a lateral crack beneath the indentation, forcing the indenter to 'pop out'.[5]

Once again, slightly more creep occurred during the 10 s dwell period at 200°C. There was, however, no evidence of cracking and considerably more elastic recovery than in the room temperature case. These results were not related to oxidation or contamination since normal room temperature behaviour was observed in the same specimen subsequent to the high temperature measurements. The relative hardness and reduced modulus data for silicon are shown alongside those for gold and glass in Table 2. As can be seen, heating led to little change in hardness, a result which is consistent with previous high temperature microhardness measurements.[6–8] However, heating did lead to a substantial reduction in reduced modulus. An interesting speculation is that an amorphous phase developed at the higher temperature, since indentation has been shown by TEM to produce some amorphous silicon.

## CONCLUSIONS

1. A novel test stage has been developed which permits routine small scale indentation and scratch testing at temperatures up to 500°C. Thermal drift problems due to convective heating and radiant heating of the displacement transducer have been effectively eliminated.

2. Indentation testing of gold and soda lime glass at 200°C revealed lower values of hardness and reduced modulus than were observed at room temperature. The results for gold were probably influenced by a change from pile-up to sinking in when the surface changed from a work hardened condition to an annealed condition.

3. Indentation testing of silicon at 200°C produced a similar hardness value to that obtained at room temperature, consistent with high temperature microhardness data reported in the literature.

4. At 200°C, silicon exhibited a significantly different indentation response to that observed at room temperature. In particular, this small rise in temperature suppressed the mechanism responsible for the well known room temperature 'pop out' event. In addition, substantially more elastic recovery occurred at the higher temperature, and this was accompanied by a reduction in reduced modulus from 140·3 to 66·0 GPa.

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