1 000 000 °C/s thin film electrical heater: *In situ* resistivity measurements of Al and Ti/Si thin films during ultra rapid thermal annealing

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We introduce a new technique for rapidly heating (10^6 °C/s) thin films using an electrical thermal annealing (ETA) pulse technique. By applying a high-current dc electrical pulse to a conductive substrate-heater material (Si), joule heating occurs thus heating the thin film. This method was demonstrated by heating thin films of aluminum at rates ranging from 10^3 to 10^6 °C/s. The temperature of the system is measured by using the substrate heater as a thermistor and is found to be within $\approx \pm 10$ °C during anneals at $\approx 10^5$ °C/s. Phase transformations in the Ti-Si system were also observed using *in situ* resistivity measurements during ETA at $\approx 10^4$ °C.

We introduce a new technique for controllable annealing thin films at ultrafast heating rates, from 10^3 to 10^6 °C/s. This is accomplished via a direct resistance heating technique referred to as electrical thermal annealing (ETA).

Many problems[1–14] in science and technology involve controlling thermally activated processes by altering the rate at which thermal annealing occurs. Several materials characterization and processing problems require high heating rates available through rapid thermal annealing (RTA) techniques, including studies in doping,[1–3] stable/metastable phase formations, and microstructure modifications.

Historically, RTA was first introduced in the electronic industry as a means to reduce crystal damage generated during the ion implantation doping process. By annealing the implanted samples at high temperatures for short periods of time, the crystal quality is recovered without excessive diffusion to the dopant. Only by annealing at high heating rates (>50 °C/s) will the recovery rate be greater than the rate of dopant diffusion. The application illustrates the core uniqueness of the RTA: The ability to control competing physical processes by means of manipulating the temperature-time characteristics of the annealed cycle.

Other examples of RTA in technology involve the selection of phase formation via rapid heating cycles. For example, in sol-gel[4] processing, the final product after annealing (pyrochlorate or perovskite) may depend on the rate of annealing. Another example is in the electronic industry during Ti silicidation for device fabrication, where two intermediate metastable phases during thermal annealing: Amorphous TiSi and $TiSi_2$(C49). It has been speculated that at high rates (>100 000 °C/s) $TiSi_2$ (C54) can be formed directly, thus reducing the thermal budget of the process.[5,6]

A variety of RTA methods have been invented for heating Si and GaAs wafers, including techniques based on proximity placement of wafers near carbon strip heaters. Presently, most commercial RTA systems use radiation-heating techniques via tungsten-halogen lamps. These systems typically have a maximum heating rate of 100–300 °C/s.

We introduce an alternative method for annealing thin films. This technique referred to as ETA generates ultrahigh heating rates by applying a high-power (≈kW) electrical pulse to a resistive heating element (Si). The thin film of interest is deposited onto the substrate prior to annealing. This substrate acts as both heating source and thermistor and is capable of measuring the temperature of the thin film at high heating rates. Heat generated within the substrate is transported to the thin film via solid-state conduction. To prevent the current which is applied to the substrate from shunting through the thin film, an electrically isolating (>20 MΩ) buffer layer of thermally grown silicon dioxide is sandwiched between the thin film and substrate.

This ETA idea is adapted from a technique often used in surface science studies, where Si is cleaned *in situ* by direct resistance heating (>1000 °C) of the Si substrate itself. However, in a more thorough literature search, we learned that this direct-heating technique had been used some 40 years earlier[7] by physicists and metallurgists for rapid heating of thin wires. This technique, which was used to study the phenomenon of "exploding" wires,[8,9] has the capability of 10^9 °C/s heating and 10^6 °C/s cooling rates.

A schematic diagram of the ETA system is shown in Fig. 1 and shows the two independent four-point probe measurements used during the cycle, one for the thin film (Al) and the other for the heater (Si). These circuits are electrically isolated by the 2-μm-thick thermal SiO_2 buffer layer.

In our experiments the substrate heaters were Si(100) wafers of resistivities 0.005 to 0.01 Ω cm having thicknesses from 75 to 400 μm and areal dimensions of ≈(0.5–1.0) cm^2. However, any conductive substrate may be used. Low resistance contacts to the Si were made via large area sintered indium pads. Joule heating of the substrate occurs during the interim when the switch (Fig. 1) is momentarily closed. Both silicon-controlled rectifier (SCR) and mechanical devices have been used for the switching component in the circuit.

The *in situ* resistivity measurement of the thin film was done via a separate four-point probe using either mechanical point contacts or lead wires with silver paste. For the experiments shown here, the substrate is almost free-standing, me-

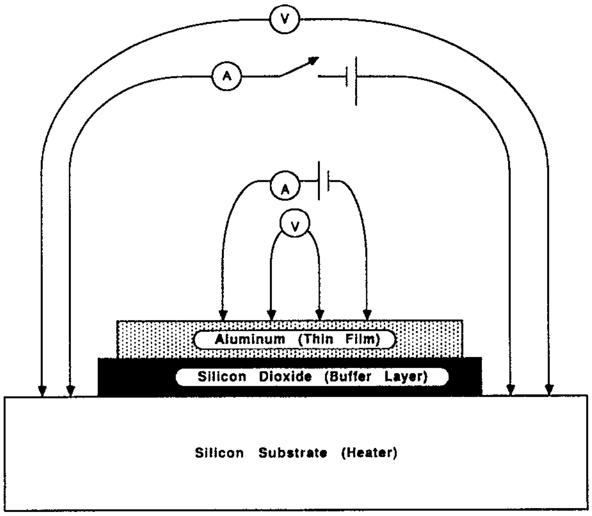

FIG. 1. Schematic diagram of the ETA system showing the four-point measurement system for the Al thin film resistivity measurement and the four-point heating/measuring circuit for the substrate (Si) heater.

chanically supported only at the ends, thus minimizing the heat loss during ETA. Data were acquired using a 100-kHz analog-to-digital converter (ADC).

Since both the thin film and buffer layer are thin (<2 μm) and have adequate thermal conductivity, the temperatures of the thin film and substrate are expected to quickly equilibrate (10^{-7} s). This was evaluated by simultaneously measuring both the temperature of an Al thin film and substrate heater using *TCR* methods. As in the case of Si, the *TCR* characteristics of the Al thin film are measured under semi-isothermal (0.1 °C/s). A comparison between the temperature of the Al thin film and substrate for an ETA experiment at a heating rate of 140 000 °C/s is shown in Fig. 2. There is excellent agreement between the two measurements, with a difference of less than 10 °C throughout most of the ETA cycle. The *TCR* temperature conversions using both (Si and Al) sets of resistance data were normalized $[R(t)/R(t=0,\ T=25\ °\mathrm{C})]$ at only one point.

Also shown in Fig. 2 are the current and voltage pulses of the Si substrate heater during the anneal. The transient behavior observed in the Al resistance (temperature) values at the beginning and end of the ETA cycle is due to the *LCR* coupling of the heater and thin film and can be minimized by applying a larger signal.

The final temperature of the sample is controlled in part by the duration of pulse. And as expected, after the pulse is completed, the system cools ($\tau \sim 0.5$ s) mainly through conduction with the ambient gases. Obviously, the rate of cooling can be dramatically increased by heat sinking the heater to a large thermal mass, helium purge, etc.

The range of annealing rates is controlled by many factors including the resistance of the substrate and contacts, the size of the power supply and the dimensions of the substrate heater. Results of a series of ETA experiments over a wide range of heating rates are shown in Fig. 3. For these experiments an adjustable power supply (a variable number of 12 V batteries arranged in series), was used to obtain heating rates ranging from 3000 °C/s to ≈1 000 000 °C/s.

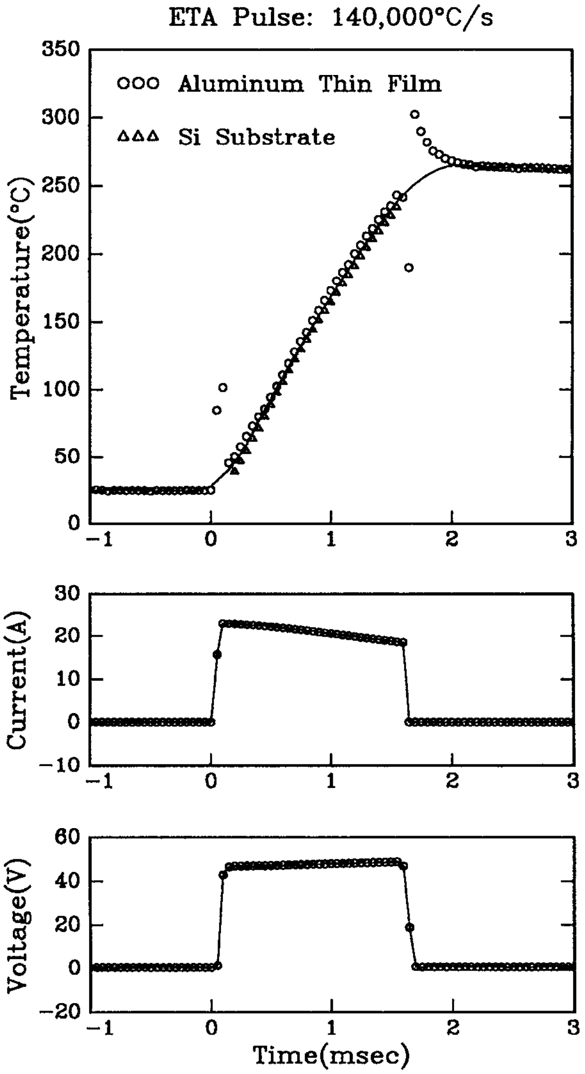

FIG. 2. Results of a 1.5-ms ETA pulse for Al film where heating rate is ≈140 000 °C/s. The top graph compares the temperature of the Al thin film with the substrate using *TCR* methods. Also shown is the current and voltage through the Si heater during the anneal.

The highest heating rate thus far obtained with the ETA system (10^6 °C/s) is extremely high, typically attained only through laser annealing. We also note that these experiments are done with an easily assembled, inexpensive (<1k$) heating apparatus, and in addition has the intrinsic capability of accurately measuring temperature. Furthermore, this system has not been optimized, heating rates of 10^7 °C/s should be easily attainable. And it may be possible, through continued development of the ETA system, to reach even higher capabilities, perhaps as high as those obtained during the annealing of thin wires:[7] 10^9 °C/s heating rates.

Besides applying the ETA technique to Al films, we also initiated experiments using it as a tool for studying phase formations. This was done using Ti polycrystalline silicon bilayers which were first deposited onto the SiO_2 layer. Shown in Fig. 4(a) are the results of an ETA experiment of

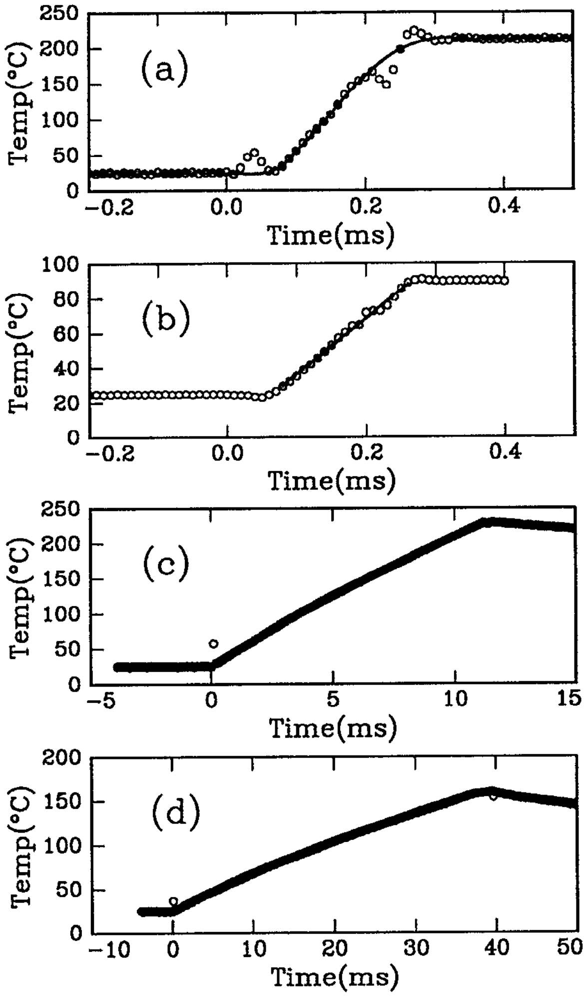

FIG. 3. ETA of Al thin film at various heating rates: (a) 1×10^6 °C/s, (b) 4×10^5 °C/s, (c) 2×10^4 °C/s, and (d) 4×10^3 °C/s. Note the initial cooling rate for these samples is ≈2000 °C/s.

the as-deposited sample annealed at ≈20 000 °C/s (100 times faster than any previously reported anneal). The two main characteristic changes in the resistance data are due to two phase formations: (i) Ti/Si⇒$TiSi_2$ (C49) and (ii) $TiSi_2$ (C49)⇒$TiSi_2$ (C54). These phases were identified in earlier work[6] using x-ray diffraction and transmission electron diffraction.[10] Also shown in Fig. 4 are the results of a similar type experiment, where $TiSi_2$ (C49) was used as the starting material, which was obtained by partially annealing the as-deposited Ti/Si sample in a conventional tube furnace at low temperatures. As expected, only one transformation was observed during the ETA anneal: $TiSi_2$ (C49)⇒$TiSi_2$ (C54).

In summary, we have introduced a new technique for rapidly heating (10^3–10^6 °C/s) thin films using an electrical thermal annealing electrical-pulse technique. This system provides not only a means of rapidly heating thin films, but also an intrinsic way to accurately measure temperature. We have demonstrated the technique by measuring the *TCR* of Al films and the phase transformations in Ti/Si system. Furthermore, the ETA system shows promise for even higher heating and cooling rates, which may be suitable for investigations of metastable compounds.

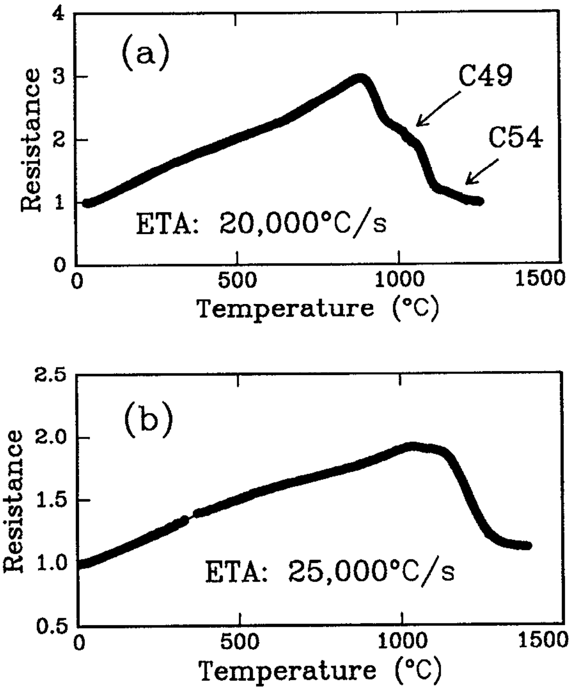

FIG. 4. *In situ* resistance measurements during silicidation of Ti/Si layers. The two transitions shown in the top figure (a) are the formation of the C49 and C54 phases of $TiSi_2$. (b) Only one transition is observed (C49⇒C54) when the starting material is C49 $TiSi_2$.

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