# Formation of a Noncrystalline Phase in Aluminum Irradiated with a Pulsed Ruby Laser

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Polycrystalline aluminum samples have been irradiated with very short (15-ns time duration) pulses from a ruby laser. After irradiation, we have detected the formation at the Al surface of a noncrystalline layer, about 1500 Å thick. This layer has been characterized by transmission electron microscopy, x-ray diffraction, and nuclear reactions. Perliminary results are also presented on the behavior of heavily Cu- and Pb-doped Al polycrystalline samples after being irradiated under the same conditions as the pure Al samples.

Amorphous phases in alloys and in some pure metals can be produced in a variety of ways, including evaporation, sputtering, electrodeposition, chemical deposition, and quenching from the liquid phase. Extensive reviews devoted to formation, structure, and properties of such phases are present in current literature.[1-6]

Splat cooling technique is based on a rapid quenching from the liquid state and is connected to a high cooling rate which leads to a supercooling of the liquid before solidification starts. If the cooling rate is high enough, the viscosity of the supercooled liquid increases continuously, as temperature decreases, hindering the formation and growth of crystalline nuclei. When the viscosity reaches a characteristic value of about $10^{13}$ P the glass transition starts and the material becomes a glassy solid (see Ref. 6 and references therein). However, with the splat cooling technique it is quite impossible to obtain amorphous phases for pure metals, even at the highest estimated cooling rates reached up to now, i.e., about $10^{10}$ °K/s.[5] Because of the high fluidity of pure metals at their equilibrium-melting temperature, only the addition of foreign atoms, in particular metalloid atoms, allows them to reach a supercooled liquid state having a large viscosity and making easier the transition to the amorphous state.

Recently laser skin melting has been used to cause surface vitrification of alloys on subsequent cooling.[7,8] With use of high-power continuously operating $CO_2$ lasers it is possible to obtain cooling rates up to about $5\times 10^8$ °K/s. In order to achieve the very high cooling rates necessary to make pure metals amorphous by thermal means, high-power, very short pulsed lasers should be used.[7]

At present there are only two works where such a facility has been used. Such works did not concern metals but a semiconductor. Amorphous silicon layers, about 300 Å thick, were obtained by irradiating silicon single crystals either with nanosecond ultraviolet-laser pulses or with picosecond pulses in the visible region.[9] In the present work we describe the results of a similar technique applied to aluminum.

In our experiment we used a $Q$-switched, 15-ns pulsed ruby laser ($\lambda = 0.694$ $\mu$m) to heat a thin layer at the surface of polycrystalline aluminum

samples with an average grain size of 2 $\mu$m. The purity of the Al specimens was better than 99.9999%. Before irradiation some samples were doped with implants of copper or lead. Implantation doses where $2\times 10^{16}$ ions/cm$^2$ at energies which were 70 and 110 keV for Cu and Pb, respectively. The projected ranges were nearly the same for both the implanted species, i.e., about 400 Å. Cu and Pb are soluble and insoluble, respectively, in the solid Al phase. Such a doping was performed to get preliminary information on the role played by the impurities in the vitrification process under study.

Laser irradiation was performed in air at room temperature. For irradiation above a threshold of about 1 J/cm$^2$, a melted layer is formed at the surface of the samples.[10] Calculations based on a simple heat-flow model show that the thickness of such a layer increases with increasing incident-energy density. For energy densities of about 3.5 J/cm$^2$, near the threshold at which the sample surface reaches the boiling temperature, the calculated melted thickness is more than 1 $\mu$m. Such depth are consistent with redistribution in depth of implanted impurities following irradiation, as a consequence of an impurity-atom diffusion into the liquid Al phase.[10]

With reference to the present work, we have used the same heat-flow model quoted above, with the same values for the relative parameters, to calculate the cooling rates of the liquid Al layer at different depths from the surface. The computer solution of the heat-diffusion equation in the laser-irradiated samples takes into account the solid/liquid phase transition, but not the liquid/vapor one. The obtained cooling rate goes through a maximum, $-\dot{T}_{max}$, at a temperature well above the melting one, going practically to zero at the melting temperature $T_M$. In order to assess the cooling rate, $-\dot{T}_{uc}$, acting when going through the melting temperature in a hypothetical undercooling process, we have repeated the calculation omitting the resolidification latent heat, and keeping the specific heat at the same value of the liquid phase. The values for $-\dot{T}_{max}$ and $-\dot{T}_{uc}$ are functions of depth and energy (see Fig. 1). For an incident energy density of 3.1 J/cm$^2$ the maximum calculated temperature at the surface layer is a little lower than the boiling one. Such a threshold value has only a qualitative significance, since it depends on the values assumed for the parameters in the model. We may therefore safely presume that the cooling rate effectively acting during our experiment for which the energy density is 3.5 J/cm$^2$, has values quite near to the ones calculated for an energy density of 3.1 J/cm$^2$.

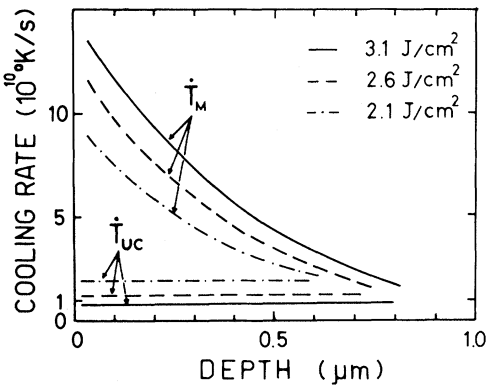


FIG. 1. Calculated cooling rates, $-\dot{T}_{max}$ and $-\dot{T}_{uc}$ vs depth of the molten layer for an aluminum sample irradiated by a 15-ns pulsed ruby laser at three different energy densities.

Laser-irradiated unimplanted and ion-implanted specimens have been analyzed by x-ray diffraction (XRD) and transmission electron microscopy (TEM). Whenever XRD results did not give structural informations about the irradiated samples, thin foils suitable for the electron microscope have been prepared by jet thinning from the backsides of the specimens and examined with a 125-kV Siemens Elmiskop 102 and a Phylips E.M. 400.

Before preparing the samples for TEM we analyzed the content of contaminants absorbed during the laser irradiation. This analysis was performed employing the 2-MeV Van de Graaff accelerator of the Istituto Nazionale di Fisica Nucleare National Laboratories of Legnaro. He-ion backscattering and $^{14}N(d,\alpha)^{12}C$ and $^{16}O(d,p)^{17}O^*$ nuclear reactions were used.

We have found no noticeable contamination by elements heavier than aluminum (our detection limits for such elements are lower than $10^{14}$ atoms/cm$^2$) although there was adsorption of nitrogen and oxygen of the order of $3\times 10^{16}$ atoms/cm$^2$. Aluminum oxides have been removed by chemical etching in hot $CrO_3$ solution.

The electron micrographs of Fig. 2(a) and the selected-area diffraction (SAD) patterns taken on pure aluminum irradiated specimens show an essentially amorphous Al film, about 1500 Å thick, on the polycrystalline substrate. In fact the inset in Fig. 2(a) shows an intensity distribution in the reciprocal space which is typical of amor-

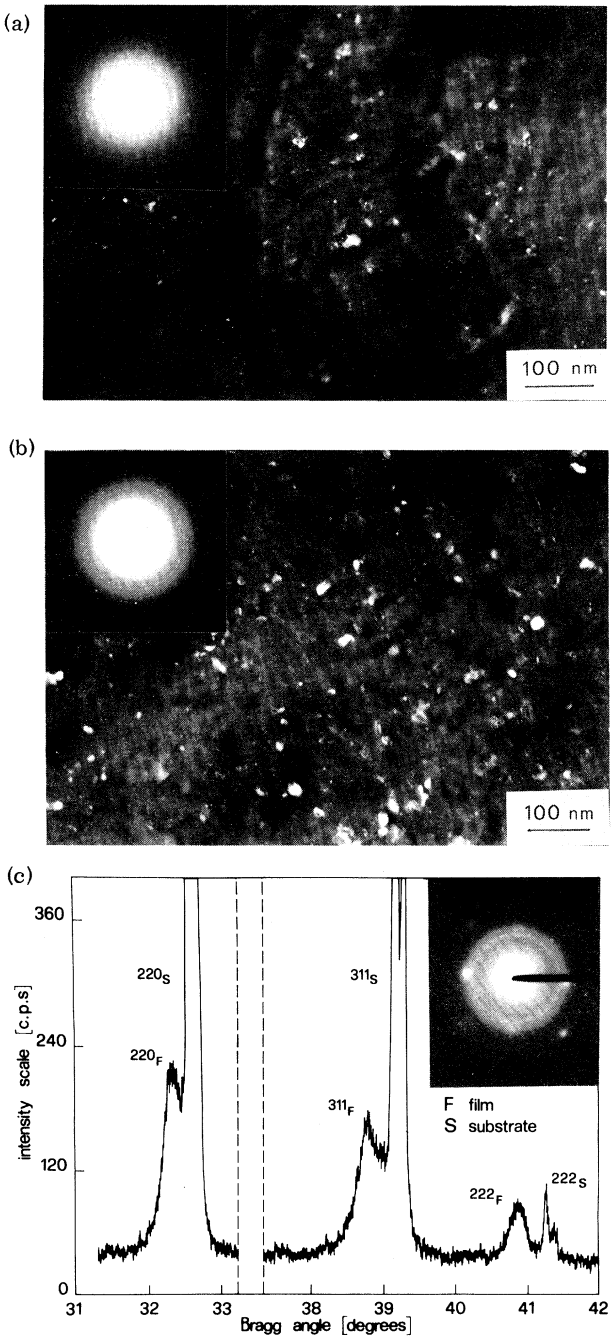


FIG. 2. (a) Dark-field electron micrograph and SAD pattern of laser-irradiated Al, showing small grains of Al and AlN embedded in the amorphous-aluminum matrix. (b) Dark-field electron micrograph and SAD pattern of Pb-implanted and laser-irradiated Al, exhibiting a situation quite similar to the one depicted in (a). (c) Part of an XRD spectrum taken with Cu $K\alpha$ radiation on Cu-implanted and laser-irradiated Al, indicating that a fine-grained, polycrystalline aluminum film has been obtained on the substrate. The SAD pattern inserted shows the absence of amorphous material.

phous material. In addition to these halos, the SAD patterns exhibit the presence of well-defined Debye rings: The experimental $d$ values obtained from these rings were found in agreement with the ones calculated for the Al and the hexagonal-AlN phases. These observations indicate that the laser irradiation has produced an amorphous Al film in which small grains of crystalline aluminum nitride are embedded [Fig. 2(a)]. The dimensions of these grains are of the order of about 100 Å.

Quite similar results have been obtained for Pb-implanted and irradiated aluminum samples. Figure 2(b) shows in fact that the formation of an amorphous aluminum film has taken place with the presence of small Al and AlN grains.

For the analysis of Cu-implanted and irradiated Al samples XRD has been successfully employed, because of the different evolution of the ion-implanted layer during the rapid cooling. In Fig. 2(c) part of a typical x-ray spectrum obtained from these specimens is reported, in which diffraction peaks corresponding to a fine-grained polycrystalline Al film are present. They are slightly shifted from the ones coming from the Al substrate. The analysis of this spectrum allows us to deduce that the size of the Al crystallites was about 250 Å and the surface layer has suffered an increase in volume of about 2.5% with respect to the substrate. The crystallinity of this layer is confirmed by the inset in Fig. 2(c), in which the presence of characteristic rings of polycrystalline Al and the absence of intensity halos due to amorphous material can be observed.

The threshold values of the cooling rate, generally accepted by the "amorphous community" of scientists, to achieve the amorphous state in pure Al are some orders of magnitude higher than the ones consistent with the simple heat-flow model quoted above. This fact seems then to suggest more complex mechanisms acting in the formation of amorphous phases under laser irradiation. Work is in progress to clarify possible evaporation and plasma-formation effects.

Pb-doped samples exhibit a behavior comparable to that shown by undoped ones. In principle the formation of an amorphous phase in Pb-doped Al should be favored in view of the increase in the viscosity of the supercooled-Al liquid caused by the addition of some metalloid atoms. We should then expect under the same irradiation conditions a thicker amorphous layer in these samples than in the undoped ones. We have not observed any such effect, within our experimen-

tal uncertainties, in this direction. We ascribe such a fact to be due to the low atomic concentration of the impurity, i.e., about 0.2 at.% in the melted thickness.

As to Cu-doped samples, we observed a very fine-grained structure with a change in the lattice constant. The presence of a crystalline structure could be explained in terms of a decrease in viscosity of pure aluminum due to the small addition of Cu impurity atoms (in our experiment the Cu concentration in the examined thickness is about 0.5 in atomic percent). Such a behavior is similar to the one observed in other metals doped with suitable metallic atoms.[11]

The increase in the lattice parameter may perhaps herald a situation very near to the crystal/glass transition. Such a transition is characterized by a volume expansion.[12] This effect is probably present in all our irradiated samples, but it is more easily detected in this case because of the crystallinity of the specimen.

Finally a transition from the amorphous to the crystalline phase was observed after annealing in vacuum at 400 °C for 30 min. Such a preliminary result obviously gives only an upper limit of the recrystallization temperature. We want to point out that the recrystallization temperature cannot be expected to coincide with some values found in annealing experiments of various defects in Al crystals; an amorphous state is not simply comparable with a crystal containing some defects. More detailed investigations are in progress to determine the crystallization behavior of the noncrystalline films we obtained.

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## Intensity of Plasmon Satellites in Ultrasoft-X-Ray Photoemission Spectra

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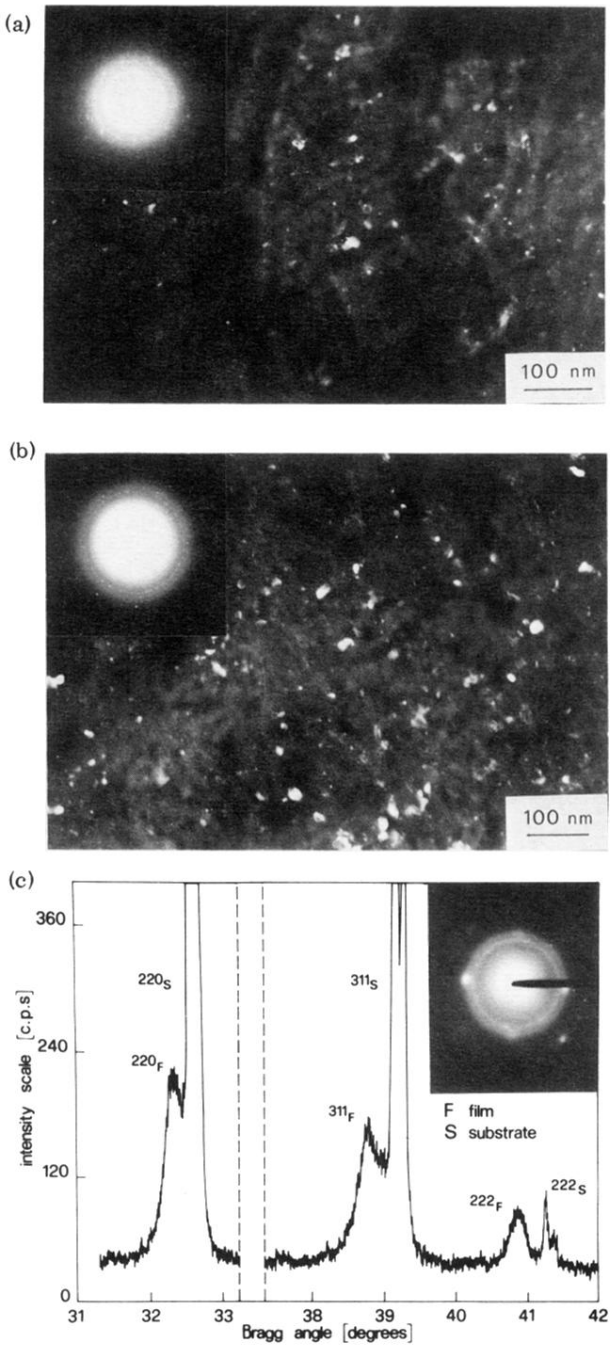
A calculation of the bulk-plasmon-satellite strengths in the photoemission spectra of metals is presented for the dispersionless plasmon model. The calculation is made for all energies, especially for the ultrasoft-x-ray regime. In this spectral region, the interference term between extrinsic and intrinsic plasmon productions is of the same order as the intrinsic production term. The photoelectron energy for which these two terms cancel each other exactly is determined.

Recently there has been a considerable interest in the observation of photoemission spectra (XPS) of metals in the *ultrasoft*-x-ray regime.[1-4] When the exciting photon energy is low enough so that the outgoing photoelectrons have an energy $\epsilon_k$ of a few times the plasmon energy $\omega_p$, there is an important weakening of the plasmon satellite intensity due to a quantum interference term between extrinsic and intrinsic plasmon production.[5] Plasmons may indeed be excited either in

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