Description

[Title of the invention]

A crystalline film production method and a crystalline film production apparatus

[Technical field]

[0001]

This invention relates to a crystalline film production method comprising irradiation of an amorphous film with a pulsed laser beam so that said amorphous film is microcrystallized to form a crystalline film, and a production apparatus therefor.

[Background art]

[0002]

To produce crystalline silicon for thin film transistors (TFTs) to be used in flat panel displays of thin-type display apparatuses such as liquid crystal display devices, either of the following two methods is generally used, one is a laser annealing where an amorphous silicon film formed on the upper layer of a substrate is irradiated with a pulsed laser beam to melt and recrystallize the film, and the other is solid phase crystallization (SPC) where a similar substrate provided with a upper layer of the amorphous silicon film is heated in a heating furnace to cause the silicon film to crystallize and grow in a solid phase without melting.

[0003]

The present inventors have verified that a fine polycrystalline film can be produced by a solid phase growth process in which a substrate is irradiated with a pulsed laser beam while maintaining a substrate in a heated state, and

proposed this process (see Patent document 1).

[Prior art references]

[Patent documents]

[0004]

Patent document 1: Japanese Unexamined Patent Publication (Kokai) No. 2008-147487

[Summary of the invention]

[Problems to be solved by the invention]

[0005]

In recent years, there is an increasing demand for methods that serve for low cost production of large sized uniform fine polycrystalline silicon films to be used for manufacturing of OLED (organic light-emitting diode) panels and LCD (liquid crystal display) panels for large TV sets.

In an organic EL display panel, which is recently regarded as likely to be next generation product to replace liquid crystal displays, organic EL element emit light itself to achieve a high screen brightness. A luminescent material of the organic EL elements is driven by a current drive mechanism, instead of a voltage drive mechanism used in LCDs, and there are different requirements for TFTs. For TFTs formed of amorphous silicon, it is difficult to depress its deterioration that takes place over time. A large drift in the threshold voltage (Vth) occurs to shorten the device life. Polysilicon, on the other hand, is a stable material with a long life. However, the variation in TFT characteristics is large in the case of TFTs fabricated with a polysilicon film. Such a variation in TFT characteristics can take place if there is a significant variation in the crystal grain size or if interfaces of crystal grains of crystalline silicon (crystal grain boundaries) exist in the TFT channel regions. The variation in TFT

characteristics tends to depend mainly on the crystal grain size and the number of the crystal grain boundaries existing between the channels. Furthermore, the electron mobility tends to increase with an increasing crystal grain size. In the case of TFTs for organic EL displays, however, as the electron mobility by electric field increases, the channel length of the TFT will have to be longer, and size of each RGB (red, green, blue) pixel will depend on the channel length of the TFT, making it impossible to achieve a high resolution. This is why there is such an increasing demand for fine crystal films with a decreased variation in crystal grain size.

[0006]

It is difficult, however, for the conventional crystallization methods to solve this problem.

The reason is that in the laser annealing process, which is one of the conventional ones, amorphous silicon is once melted and then recrystallized, and the crystal grains formed tend to be large in diameter and also large in the variation in crystal grain size. Accordingly, the electron mobility by electric field will be high as described above, and there will be a variation in the number of crystal grains in those TFT channel regions. In addition, these crystal grains will have random shapes and adjacent crystals will have different crystal orientations. As a result, these will have large influence on the variation in TFT characteristics. In particular, differences of crystallinity are likely to take place in regions where laser irradiation overlaps, and these crystallinity differences can have large influence on the variation in TFT characteristics. In addition, another problem can take place due to crystal defects caused by surface contamination (impurities).

[0007]

The crystals produced by the solid phase crystallization process (SPC process) are small in grain size and also small in TFT variation, indicating that

it is the most effective crystallization method to solve the aforementioned problem. However, it requires a long crystallization time, and it is difficult to apply to mass production. A batch-type heat treatment apparatus for simultaneous processing of a number of substrates is used in a heat treatment step that can perform the solid phase crystallization process (SPC). As many substrates are heated simultaneously, the heating and cooling time increases and the temperature tend to be ununiform in the substrates. If heating is continued for a long period of time at a high temperature above the strain point temperature of the glass substrates in the solid phase growth process, the glass substrates themselves will suffer shrinkage or expansion to cause damage to the glass. In the SPC process, the crystallization temperature is higher than the glass transition point, and a small temperature distribution can lead to deflection and shrinkage distribution in the glass substrates. As a result, even if crystallization is possible, troubles can take place in exposure and other steps, making it difficult to prepare devices. Temperature uniformity is more required with increasing in a processing temperature. In general, the crystallization speed depends on the heating temperature, and a processing time of 10 to 15 hours is required at 600°C, 2 to 3 hours is required at 650°C, and several tens of minutes is required at 700°C. A long processing time is necessary to perform processing without causing damage to the glass substrates, making it difficult to use this method for mass production.

[0008]

The present invention has been accomplished in such background circumstances and it is an object of the present invention to provide a crystalline film production method in which a fine crystalline film with a small variation in crystal grain size is produced efficiently from an amorphous film without causing damage to the substrate.

[Means of solving the problems]

[0009]

Specifically, the first aspect of the crystalline film production method of the present invention comprises irradiating an amorphous film formed on a substrate with 1 to 10 shots of a pulsed laser beam with a wavelength of 340 to 358 nm and an energy density of 130 to 240 mJ/cm^2 so that said amorphous film is heated at a temperature not in excess of a crystalline melting point and said amorphous film is crystallized.

[0010]

The crystalline film production apparatus of the present invention comprises a pulsed laser beam source to emit a pulsed laser beam with a wavelength of 340 to 358 nm, an optical system to lead said pulsed laser beam to an amorphous film for irradiation, an attenuator to adjust the attenuation rate of said pulsed laser beam emitted from said pulsed laser beam source so that said laser beam has an energy density of 130 to 240 mJ/cm^2 at the surface of the amorphous film, and a scanning apparatus to move said laser beam relatively to said amorphous film so that overlapping irradiation of said amorphous film with said pulsed laser beam is performed in the range of 1 to 10 shots.

[0011]

According to the present invention, a pulsed laser beam in a ultraviolet wavelength range with a moderate energy density is applied to an amorphous film with a moderate number of shots to achieve rapid heating so that the amorphous film is heated up to a temperature not in excess of the crystalline melting point to allow uniform fine crystallites with little grain size variation, for instance, protrusion-free fine crystallites with a size of 50 nm or less, to be produced by a process that is different from the conventional melting and recrystallization process. The resulting crystal grains will grow up to a

diameter of larger than 50 nm when the conventional melting and crystallization processes are used, and the crystal grains will have a large variation and fail to form fine crystals when the melting and crystallization processes or SPC (solid phase crystallization) process using a heating furnace is carried out.

According to the present invention, furthermore, the amorphous film to be crystallized will not undergo further phase change since the amorphous film is heated only up to a temperature not in excess of the crystalline melting point. For instance, only the amorphous silicon regions are converted into crystal silicon, so the regions where the pulsed laser beam irradiation overlaps will have the same crystallinity as in other regions, leading to an improved uniformity. Here, the irradiation with a pulsed laser beam under the conditions according to the present invention can heat the amorphous film up to a higher temperature compared to the conventional solid phase crystallization process.

[0012]

Use of a pulsed laser beam instead of a continuous-wave laser beam serves to prevent the underlying substrate from being heated up to a temperature at which it can be damaged. The present invention does not require the heating of the substrate itself, but the present invention may not eliminate the heating of the substrate. It is desirable for the present invention, however, to perform said pulsed laser beam irradiation without heating the substrate.

[0013]

Here, if the amorphous film formed on the substrate has high hydrogen content and is irradiated with high energy such as by the melting and crystallization process, the Si-H molecular bond is likely to break and undergo ablation, leading to dehydrogenation. When the process of the invention is used, the amorphous silicon is converted in the solid phase without easily undergoing

ablation, making it possible to process a non-dehydrogenated amorphous film.

Described below is the conditions specified for the invention.

[0014]

Wavelength range: 340 to 358 nm

A laser beam in the above wavelength range is absorbed efficiently by an amorphous film, particularly by an amorphous silicon film, and a pulsed laser beam in said wavelength range can directly heat an amorphous film. This eliminates the need to indirectly provide a laser absorption layer on the amorphous film. Because the laser beam is sufficiently absorbed by the amorphous film, furthermore, it is possible to prevent the substrate from being heated by the laser beam and thus prevent the substrate from suffering damage due to deflection or deformation of the substrate.

Here, if the laser beam used is in such a wavelength range that the laser beam can transmit an amorphous film, particularly an amorphous silicon film, though absorbed partially by the amorphous film, multiple reflection will take place from a under layer,. And therefore, the light absorption rate in the irradiated portions of the amorphous film will depend largely on deviation (variation) in the thickness of the under layer below the amorphous film. A laser beam in the aforementioned wavelength range is completely absorbed at the surface layer of the amorphous film, particularly in the case of the silicon film. Thus, it is not necessary to take into serious consideration the variation in the thickness of the under layer in producing a polycrystalline film. As the transmission through the amorphous film can be virtually ignored, furthermore, this method can be applied also to an amorphous film formed on a metal surface.

[0015]

In case of crystallization carried out by using a laser beam with a wavelength in the visible range, a silicon layer with a thickness of 50 nm or so

not only absorbs it but also partially transmits it, resulting in multiple reflection from the under layer below the silicon (i.e., buffer layer of such as SiO2 layer, SiN layer etc.), which will have an undesired influence. Specifically, the light absorption rate will vary if the buffer layer below the silicon layer does not have a uniform thickness. A similar problem will also take place with the method that uses a capping layer of SiO2 layer etc. on the silicon layer.

In case where a pulsed laser beam with a wavelength in the infrared range is used, a silicon layer with a thickness of 50 nm or so will hardly absorb the laser beam, and therefore, a light absorbing layer is commonly provided on the silicon. If the present case is applied, however, it naturally requires a step to form a light absorbing layer and a step to remove it after the pulsed laser beam irradiation.

In view of these, the present invention requires the use of a pulsed laser beam with a wavelength in the ultraviolet range of 340 to 358 nm.

[0016]

Energy density: 130 to 240mJ/cm^2

If an amorphous film is irradiated with a pulsed laser beam with an appropriate degree of energy density (at the amorphous film), the amorphous film will crystallize in the solid phase or after being heated to a temperature above the melting point of the amorphous and not in excess of the crystalline melting point,. leading to formation of fine crystal. If the energy density is lower, the amorphous film will not be heated sufficiently up to a required temperature, leading to insufficient crystallization or making it difficult to achieve crystallization. If the energy density is higher, on the other hand, melt crystallization or an ablation will occur. Thus, the pulsed laser beam used should have an energy density in the range of 130 to 240mJ/cm^2.

[0017]

The number of shots: 1 to 10

For irradiation of an amorphous film with a pulsed laser beam, the number of shots in one region is prescribed appropriately. If the energy varies over the area of the irradiating beam, implementation of irradiation in two or more shots allows the crystallization temperatures to be averaged, making it possible to produce uniform fine crystallites.

If the number of shots is too large, the amorphous film can be heated up to above the crystalline melting point, possibly causing melting or ablation. With an increasing number of shots, furthermore, a longer processing time will be required, leading to a lower efficiency.

[0018]

Degree of crystallinity: 60 to 95%

It is preferable that the degree of crystallinity is adjusted to 60 to 95% under the aforementioned conditions for wavelength, energy density, and number of shots. If the degree of crystallinity is less than 60%, it will be difficult to develop a film with good characteristics to be used in thin film transistors, etc. A degree of crystallinity of 60% or more will not be achieved if the amorphous film are not deposited a sufficient energy. If the degree of crystallinity is more than 95%, on the other hand, the crystallite size will become large, making it difficult to produce fine, uniform crystallites. The degree of crystallinity will easily exceed 95% if pulsed laser beam irradiation continues above the crystalline melting point.

The degree of crystallinity is specifically determined from the area of the crystalline peak and that of the noncrystalline peak in Raman spectrometry (peak area of crystalline Si/ (peak area of noncrystalline Si + peak area of crystalline Si)).

[0019]

Here, it is preferable that the pulse width (half-width) of the pulsed laser beam used is in the range of 5 to 100 ns. If the pulse width is too small,

the maximum power density will increase to heat the film up to a temperature above the melting point, possibly causing melting or ablation. If the pulse width is too large, the maximum power density will decrease, possibly failing to achieve heating up to a temperature where solid phase crystallization can take place.

[0020]

It is preferable, furthermore, that the pulse frequency of the pulsed laser beam used is in the range of 6 to 10 kHz.

A pulsed laser beam with an appropriately high pulse frequency (6 kHz or more) will serve for efficient crystallization because the shot interval can be shortened and the heat developed by pulsed laser beam irradiation can be retained in the amorphous film. An excessively high pulse frequency, on the other hand, is likely to cause melting and ablation.

[0021]

It is preferable that the short axis width of said pulsed laser beam is in the range of 1.0 mm or less.

Scanning the pulsed laser beam in the direction of the short axis width relatively to the amorphous film serves for crystallization over a large region while irradiating and heating particular parts of the amorphous film. If the short axis width is too large, the scanning speed has to be increased for efficient crystallization, leading to larger equipment cost.

[0022]

Scanning the pulsed laser beam relatively to the amorphous film allows said amorphous film to crystallize in the plane direction. Said scanning may be achieved by moving the pulsed laser beam, moving the amorphous film, or moving both. Said scanning is preferably performed at a speed of 50 to 1000 mm/sec.

If this scanning speed is too small, the maximum power density will

increase to heat the amorphous film up to a temperature above the crystalline melting point, possibly causing melting or ablation. If the scanning speed is too large, the maximum power density will decrease, possibly failing to achieve heating up to a temperature where solid phase crystallization can take place.

[0023]

Here, the production apparatus of the present invention uses a solid-state laser source to produce a pulsed laser beam in the ultraviolet range, serving to emit a pulsed laser beam in an intended wavelength range. The laser beam source with high maintainability can be incorporated for efficient fine crystallite formation. It is possible to irradiate an amorphous film with a pulsed laser beam after appropriate energy density adjustment by an energy adjustment device to ensure production of uniform, fine crystals. The energy adjustment device may be designed so that the output of the solid-state laser source is controlled to achieve a predetermined energy density, or the attenuation rate of the pulsed laser beam emitted from the solid-state laser source is controlled for energy density adjustment. Said pulsed laser beam is relatively scanned, by a scanning apparatus, to the amorphous film to allow fine, uniform crystals to be produced at an appropriate degree of crystallinity in large regions of the amorphous film. The scanning serves to set an appropriate pulse frequency, short axis width of the pulsed laser beam, and scanning speed so that the number of shots in one region of the amorphous film is 1 to 10.

Said scanning apparatus may be designed so that the pulsed laser beam is moved by moving the optical system that collimates the pulsed laser beam or by moving the table mounting the amorphous film.

[Effect of the invention]

[0024]

Thus, as described above, the method of the present invention serves to

heat an amorphous film to crystallize it at a temperature not in excess of the crystalline melting point by preparing an amorphous film on a substrate layer and applying 1 to 10 shots of pulsed laser beam irradiation with a wavelength of 340 to 358 nm and energy density of 130 to 240 mJ/cm^2. To solve the aforementioned problem, the present invention can produce an extremely uniform film that contains crystals with such a small average grain size that two or more crystal grains can be incorporated in a TFT channel region. In recently developed TFTs, the line width is becoming smaller and the size of the regions for channel formation (channel length, channel width) is also becoming smaller. Accordingly, there is an increasing demand for a method that can allow a stable crystalline film with a small average grain size to be produced uniformly over the entire surface of a substrate. In particular, there is increasing need for a crystallization technique that can minimize the difference in TFT characteristics between adjacent regions, and this need can be fully met by the present invention. In addition, this also serves to remove impurities from the film surface.

According to the present invention, furthermore, the cost for both equipment and maintenance can be reduced, leading to an increased operating rate for the processing, and in turn, an increased productivity.

[0025]

The process of the present invention can perform processing at a temperature not in excess of the transition point of the substrate (glass etc.), or at a considerably low temperature even in cases where it is above the transition point, allowing only the amorphous film to be crystallized by applying a laser beam to heat it up to a high temperature. At the same time, it also serves to produce crystallites with size of 50 nm or less quickly. In addition, crystallites with size of 50 nm or less can be produced in regions where laser irradiation overlaps (effective for production of large area crystallization).

Moreover, it can minimize the shape changes in the substrate (deflection, deformation, internal stress). The substrate is slightly heated at the same time, serving to remove impurities existing in the amorphous film and contamination on its surface.

Brief description of the drawings

[0026]

[Figure 1] This shows a longitudinal section of a solid-state ultraviolet laser annealing apparatus that constitutes a production apparatus in an embodiment of the present invention.

[Figure 2] Similarly, this shows SEM photographs of thin films irradiated with a pulsed laser beam under various production conditions in Examples.

[Figure 3] Similarly, this shows SEM photographs of thin films irradiated with a pulsed laser beam under various production conditions in other Examples.

[Figure 4] Similarly, this shows SEM photographs of thin films irradiated with a pulsed laser beam under various production conditions in other Examples.

[Figure 5] Similarly, this shows results of Raman spectrometry.

[Best mode for carrying out the invention]

[0027]

An embodiment of the present invention is described below with reference to Figure 1.

The crystalline film production method of this embodiment focuses on a substrate 8 to be used in the TFT device in a flat panel display, and as an amorphous film, a thin amorphous silicon film 8a has been formed on said substrate 8. The thin amorphous silicon film 8a is formed with a common method on the substrate 8, and dehydrogenation is omitted.

This description, however, is not intended to limit the properties of the

substrate or amorphous film used for the present invention.

[0028]

Figure1 shows a solid-state ultraviolet laser annealing apparatus 1 used for the crystalline film production method in the embodiment of the present invention. The solid-state ultraviolet laser annealing apparatus 1 works as the crystalline film production apparatus of the invention.

The solid-state ultraviolet laser annealing apparatus 1 comprises a solid-state ultraviolet laser oscillator 2 that emits a pulsed laser beam with wavelength of 340 to 358 nm, pulse frequency of 6 to 10 kHz, and pulse width 5 to 100 ns, installed on a vibration-free base 6, and said solid-state ultraviolet laser oscillator 2 provides a control circuit 2a to produce pulse signals.

[0029]

An attenuator (attenuation unit) 3 is provided on the output side of the solid-state ultraviolet laser oscillator 2, and an optical fiber cable 5 is connected to the output side of the attenuator 3 via a coupler 4. The transmitting end of the optical fiber cable 5 is connected to an optical system 7 that comprises condenser lenses 70a and 70b, and beam homogenizers 71a and 71b, etc., provided between the condenser lenses 70a and 70b. On the outgoing side of the optical system 7, a substrate placing table 9 is installed for placing the substrate 8. The optical system 7 is set up so that it shapes a pulsed laser beam into a rectangular or linear beam with a short axis width of 1.0 mm or less.

Said substrate placing table 9 is movable in the plane direction (X-Y direction) of the substrate placing table 9, and provided with a scanning apparatus 10 for high speed movement of the substrate placing table 9 in said plane direction.

[0030]

Described below is a thin amorphous silicon film crystallization method using said solid-state ultraviolet laser annealing apparatus 1.

First, the substrate placing table 9 carries a substrate 8 on which a layer of thin amorphous silicon film 8a is formed. In this embodiment, heating of said substrate 8 with a heater etc. is not performed.

The control circuit 2a generates pulse signals to produce a pulsed laser beam with a prescribed pulse frequency (6 to 10 kHz) and a pulse width of 5 to 100 ns. , and the pulse signals are used by the solid-state ultraviolet laser oscillator 2 to emit a pulsed laser beam with a wavelength of 340 to 358 nm.

[0031]

The pulsed laser beam emitted from the solid-state ultraviolet laser oscillator 2 reaches the attenuator 3 and attenuated at a predetermined attenuation rate while passing through the attenuator 3. Said attenuation rate is adjusted so that the pulsed laser beam will have an energy density required for the present invention at the processing plane. The attenuator 3 may be of a variable attenuation rate type.

The pulsed laser beam with an adjusted energy density is transmitted through the optical fiber cable 5 and introduced into the optical system 7. In the optical system 7, the pulsed laser beam is shaped by the condenser lenses 70a and 70b and beam homogenizers 71a and 71b, etc., into a rectangular or linear beam with a short axis width of 1.0 mm or less, which is emitted toward the substrate 8 to achieve irradiation with an energy density of 130 to 240 mJ/cm^2 at the processing plane.

[0032]

Said substrate placing table 9 is moved by the scanning apparatus 10 in the short axis direction of said linear beam along the surface of the thin amorphous silicon film 8a. As a result, a large region of the surface of the said thin amorphous silicon film 8a is irradiated with relative scanning by said pulsed laser beam. Here, the speed of movement by the scanning apparatus is adjusted so that the scanning speed of the pulsed laser beam is 50 to 1000

mm/sec, and 1 to 10 shots of overlapping irradiation of the pulsed laser beam are applied to one region of the thin amorphous silicon film 8a. Said number of shots is determined based on the frequency of said pulse, pulse width, short axis width of the pulsed laser beam, and scanning speed of the pulsed laser beam.

[0033]

Said irradiation with the pulsed laser beam serves to heat only the thin amorphous silicon film 8a on the substrate 8 to achieve quick polycrystallization. During this step, the thin amorphous silicon film 8a is heated at a temperature not in excess of the crystalline melting point (for instance, above 1000°C to about 1400°C). The heating can be performed either at a temperature not in excess of the amorphous melting point, or at a temperature above the amorphous melting point and not in excess of the crystalline melting point.

The thin crystalline film produced by said irradiation contains uniform, fine, high-quality crystals with a crystal grain size of 50 nm or less and free of protrusions such as those resulting from the conventional solid phase crystal growth process. Typical preferable ones include those with an average grain of 20 nm or less and a standard deviation of 10 nm or less. The crystal grain size can be measured by the atomic force microscopy (AFM). The degree of crystallinity of the resulting crystals can be calculated from the ratio between the crystalline peak area and the noncrystalline peak area determined by the Raman spectroscopy. Said degree of crystallinity is preferably 60 to 95%.

Said thin crystalline film can be used effectively as material for organic EL displays. The present invention, however, is not limited to these uses and can be useful for other liquid crystal displays and electronic materials.

The substrate placing table in said embodiment moves in order to perform relative scanning of pulsed laser beam, but instead, the optical system

that collimates the pulsed laser beam may be moved at a high speed to perform such relative scanning of a pulsed laser beam.

Example 1

[0034]

Described below are Examples of the present invention in comparison with Comparative examples.

An experiment was carried out, in which a thin amorphous silicon film formed on the surface of a glass substrate with a common method was irradiated with a pulsed laser beam using the solid-state ultraviolet laser annealing apparatus 1 as described in said embodiment.

The pulsed laser beam used in said experiment had a wavelength of 355 nm in the ultraviolet range, a pulse frequency of 8 kHz, and a pulse width of 80 nsec. The energy density was adjusted to an intended energy density value by controlling the attenuator 3.

The pulsed laser beam was shaped by the optical system so that it is circular at the processing plane, and the amorphous silicon film on the substrate was irradiated with the pulsed laser beam under various conditions for the energy density, beam size, and number of shots at the processing plane. The amorphous silicon was heated and converted into crystal silicon. Evaluation of this irradiated thin film was carried out based on SEM photographs as shown in Figure 2. The conditions and evaluation results are shown in Table 1.

[0035]

When a pulsed laser beam with an energy density of 70mJ/cm^2 was used for irradiation of a thin film, crystals of 10 to 20 nm as shown in Photograph 1 were produced after 8000 shots. This process, however, was not industrially useful because the number of shots was too large and a long period

of processing time was required.

On the other hand, crystallization of a thin amorphous film was not achieved at an energy density of 70 mJ/cm^2 and 800 shots. This is because the energy density was too low to cause crystallization even at an increased number of shots.

Subsequently, when the energy density of the pulsed laser beam was increased to 140, 160, 180, and 200mJ/cm^2, uniform and fine crystals were produced as shown in Photograph 2 to 6.

Subsequently, when the energy density of the pulsed laser beam was increased to 250mJ/cm^2, the film was heated up to a temperature above the crystalline melting point and melted into a melt-crystallized state, failing to develop fine crystals, as shown in Photograph 7.

Ablation took place as shown in Photograph 8 when the energy density of the pulsed laser beam was further increased to 260mJ/cm^2.

Thus, production of uniform and fine crystals is possible only when the conditions for the energy density of the pulsed laser beam, pulse width, and number of shots were set up appropriately.

[0036]

As obvious from these photographs, the thin polycrystalline silicon film produced by the method of the present invention was small in crystal grain size variation and uniformly polycrystallized over the entire surface, indicating that it was a high quality thin polycrystalline silicon film. At the same time, it was also found that similar uniform crystallites were formed in regions subjected to overlapping irradiation. The crystal grains were small, i.e. 50 nm or less, and free of protrusions. Thus, uniform and fine crystalline silicon films were produced, indicating that it was possible to provide silicon films with little variation in TFT characteristics.

[0037]

[Table 1]

Energy density (mJ/cm^2)	70	70	140	160	160	180	200	250	260
Beam size	1 mm dia.	1 mm dia.	1 mm dia.	0.1 mm dia.	0.1 mm dia.	0.1 mm dia.	0.1 mm dia.	0.1 mm dia.	0.1 mm dia.
Number of shots	8000	800	4	1	2	1	1	1	1
SEM photograph	Photograph 1	-	Photograph 2	Photograph 3	Photograph 4	Photograph 5	Photograph 6	Photograph 7	Photograph 8
State	Uniform, fine crystal	not crystallized	uniform, fine crystal	uniform, fine crystal	uniform, fine crystal	uniform, fine crystal	uniform, fine crystal	melt-crystallized	ablated

[0038]

Described below are other Examples of the present invention in comparison with Comparative examples.

An experiment was carried out, in which a thin amorphous silicon film formed on the surface of a glass substrate with a common method was irradiated with a pulsed laser beam using the solid-state ultraviolet laser annealing apparatus 1 as described in said embodiment. The pulsed laser beam used in said experiment had a wavelength of 355 nm in the ultraviolet range, a pulse frequency of 6 to 8 kHz, and a pulse width of 80 ns (nsec). The pulse energy density was adjusted to an intended energy density value by controlling the attenuator 3. The number of shots was adjusted to an intended number controlling the stage speed. The energy density and the number of shots used for the various test specimens are shown in Table 2. The measurements of the degree of crystallinity made below are also shown in Table 2.

The pulsed laser beam was shaped by the optical system so that it is rectangular at the processing plane, and the amorphous silicon film on the substrate was irradiated. The amorphous silicon was heated and converted into crystal silicon. Evaluation of this irradiated thin film was carried out based on SEM photographs as shown in Figures 3 and 4 and Raman spectrometry as shown in Figure 5. The degree of crystallinity was calculated from Raman spectrometry according to an equation (1): peak area of crystalline Si/(peak area of noncrystalline Si + peak area of crystalline Si).

Specifically, in the following Examples and Comparative examples, Raman spectrometry was carried out for thin film specimens with a thickness of 50 nm by irradiating of an Ar ion laser beam with a wavelength of 514.5 nm and output of 2 mW condensed to a 1 mm diameter. The results of Raman spectrometry shown in Figure 5 indicate that a sharp peak of crystal Si exists near 520 cm^{-1} while there exists no significant peak for amorphous Si near

480 cm-1.

Furthermore, Gaussian fitting was performed with the least square method to separate two peak waveforms, and these peaks were substituted in said equation (1) to calculate the degree of crystallinity.

Figure 5 shows results of Example 3 described below and the result of above calculations indicate that the degree of crystallinity is about 88%.

[0039]

(Example 2)

A pulsed laser beam was adjusted to have an energy density of 130mJ/cm^2 and a pulse frequency of 6 kHz. Fine crystallites with a diameter of 10 to 20 nm were formed in a thin film irradiated with 6 shots of said pulsed laser beam, as shown in Photograph 10. Raman spectrometry indicated that the degree of crystallinity was 85%. Similar results were obtained when the pulse frequency was adjusted to 8 kHz.

[0040]

(Example 3)

A pulsed laser beam was adjusted to have an energy density of 140mJ/cm^2 and a pulse frequency of 6 kHz. Fine crystallites with a diameter of 10 to 20 nm were formed in a thin film irradiated with 6 shots of said pulsed laser beam, as shown in Photograph 11. Raman spectrometry indicated that the degree of crystallinity was 88%. Similar results were obtained when the pulse frequency was adjusted to 8 kHz.

[0041]

(Example 4)

A pulsed laser beam was adjusted to have an energy density of 150mJ/cm^2 and a pulse frequency of 6 kHz. Fine crystallites with a diameter of 10 to 20 nm were formed in a thin film irradiated with 6 shots of said pulsed laser beam, as shown in Photograph 12. Raman spectrometry indicated that

the degree of crystallinity was 90%. Similar results were obtained when the pulse frequency was adjusted to 8 kHz.

[0042]

(Example 5)

A pulsed laser beam was adjusted to have an energy density of 160mJ/cm^2 and a pulse frequency of 6 kHz. Fine crystallites with a diameter of 20 to 30 nm were formed in a thin film irradiated with 6 shots of said pulsed laser beam, as shown in Photograph 13. Raman spectrometry indicated that the degree of crystallinity was 90%. Similar results were obtained when the pulse frequency was adjusted to 8 kHz.

[0043]

(Example 6)

A pulsed laser beam was adjusted to have an energy density of 180mJ/cm^2 and a pulse frequency of 6 kHz. Fine crystallites with a diameter of 20 to 30 nm were formed in a thin film irradiated with 6 shots of said pulsed laser beam, as shown in Photograph 14. Raman spectrometry indicated that the degree of crystallinity was 95%. Similar results were obtained when the pulse frequency was adjusted to 8 kHz.

[0044]

(Example 7)

A pulsed laser beam was adjusted to have an energy density of 200mJ/cm^2 and a pulse frequency of 6 kHz. Fine crystallites with a diameter of 40 to 50 nm were formed in a thin film irradiated with 6 shots of said pulsed laser beam, as shown in Photograph 15. Raman spectrometry indicated that the degree of crystallinity was 95%. Similar results were obtained when the pulse frequency was adjusted to 8 kHz.

[0045]

(Comparative example 1)

A pulsed laser beam was adjusted to have an energy density of 250mJ/cm^2 and a pulse frequency of 6 kHz. A thin film irradiated with 6 shots of said pulsed laser beam was heated up to a temperature above the melting point and converted into a melt-crystallized state, failing to develop uniform crystals, as shown in Photograph 16. Raman spectrometry indicated that the degree of crystallinity was 97%. Similar results were obtained when the number of shots was decreased to 1.

[0046]

(Comparative example 2)

A pulsed laser beam was adjusted to have an energy density of 260mJ/cm^2 and a pulse frequency of 6 kHz. A thin film irradiated with 6 shots of said pulsed laser beam suffered ablation as shown in Photograph 17.

[0047]

(Comparative example 3)

A pulsed laser beam was adjusted to have an energy density of 120mJ/cm^2 and a pulse frequency of 8 kHz. Crystallization actually took place in a thin film irradiated with 8 shots of said pulsed laser beam. Some crystalline parts were etched undesirably, however, when the film was subjected to a Secco etching process, as shown in Photograph 18. Raman spectrometry indicated that the degree of crystallinity was 54%.

[0048]

(Example 8)

A pulsed laser beam was adjusted to have an energy density of 160mJ/cm^2 and a pulse frequency of 8 kHz. Fine crystallites with a diameter of 10 to 20 nm were formed in a thin film irradiated with 2 shots of said pulsed laser beam, as shown in Photograph 19. Raman spectrometry indicated that the degree of crystallinity was 75%.

[0049]

(Example 9)

A pulsed laser beam was adjusted to have an energy density of 180mJ/cm^2 and a pulse frequency of 8 kHz. Fine crystallites with a diameter of 10 to 20 nm were formed in a thin film irradiated with 2 shots of said pulsed laser beam, as shown in Photograph 20. Raman spectrometry indicated that the degree of crystallinity was 78%.

[0050]

(Comparative example 4)

A similar experiment was carried out with a different laser from that used in above experiment, that is, a XeCl excimer laser that produces a beam with a wavelength of 308 nm and a pulse width of 20 nsec. The pulsed laser beam was adjusted to have an energy density of180 mJ/cm^2 and a pulse frequency of 300 Hz. A thin film was crystallized with 8 shots of pulsed laser beam irradiation and then subjected to a Secco etching process for SEM observation. As a result, the crystalline parts were etched entirely. Raman spectrometry indicated that the degree of crystallinity was 54%. This suggests that crystallization took place only in the surface layer because the wavelength of the beam was short.

[0051]

(Comparative example 5)

A similar experiment was carried out with a different laser from that used in above experiment, that is, a XeCl excimer laser that produces a beam with a wavelength of 308 nm and a pulse width of 20 nsec. The pulsed laser beam was adjusted to have an energy density of 200mJ/cm^2 and a pulse frequency of 300 Hz. A thin film irradiated with 8 shots of said pulsed laser beam was heated up to a temperature above the crystalline melting point and converted into a melt-crystallization, failing to develop uniform crystals, as shown in Photograph 21. Raman spectrometry indicated that the degree of

crystallinity was 97%.

[0052]

[Table 2]

Specimen No.	Comparative example	Example								Comparative example			
	3	2	3	4	5	8	9	6	7	1	2	4	5
Wavelenghth/ pulse width	355 nm/ 80 ns	355 nm/80 ns								355 nm/80 ns		308 nm/20 ns	
Pulse frequency	8 kHz	6 kHz				8 kHz		6 kHz		6 kHz		300 Hz	
Energy density (mJ/cm^2)	120	130	140	150	160	160	180	180	200	250	260	180	200
Number of shots (shots)	8	6	6	6	6	2	2	6	6	6	6	8	8
SEM photograph	Photograph 18	Photograph 10	Photograph 11	Photograph 12	Photograph 13	Photograph 19	Photograph 20	Photograph 14	Photograph 15	Photograph 16	Photograph 17	-	Photograph 21
Degree of crystallinity (%)	54	85	88	90	90	75	78	95	95	97	-	54	97
Crystal grain size (nm)	5	10 to 20	10 to 20	10 to 20	20 to 30	10 to 20	10 to 20	20 to 30	40 to 50	100 or more	-	-	-
State	partially crystallized	Fine crystallites formed	Fine crystallites formed	Fine crystallites formed	Fine crystallites formed	Fine crystallites formed	Fine crystallites formed	Fine crystallites formed	Fine crystallites formed	melt-crystallized	ablated	melt-crystallized	melt-crystallized

[0053]

The average grain size was 15 nm and the standard deviation σ was 7 nm in Example 3. The average crystal grain size was 72 nm and the standard deviation σ was 42 nm in Comparative example 1.

[0054]

As obvious from Figure 5 and the photographs in Figures 3 and 4, the thin polycrystalline silicon films produced according to the present invention were small in the crystal grain size variation and high in the degree of crystallinity. It was also found that they were uniformly polycrystallized over the entire surface, and that similar uniform crystallites were formed in regions subjected to overlapping laser irradiation. The crystal grains were small, i.e. 50 nm or less, and free of protrusions. Thus, uniform crystalline silicon films were produced, indicating that it is possible to provide silicon films with small variation in TFT characteristics.

[0055]

Thus, the present invention has been described with reference to said embodiment and Examples, but the invention is not limited to the scope of said description. It is naturally possible to make appropriate changes as long as they do not deviate from the scope of the present invention.

Explanation of numerals

[0056]

1 solid-state ultraviolet laser annealing apparatus

2 solid-state ultraviolet laser oscillator

3 attenuator (attenuation unit)

4 coupler

5 optical fiber cable

6 vibration-free base

7	optical system
70a	condenser lens
70b	condenser lens
71a	beam homogenizer
71b	beam homogenizer
8	substrate
8a	thin amorphous silicon film
9	substrate placing table
10	scanning apparatus

CLAIMS

[Claim 1]

A crystalline film production method comprising irradiating an amorphous film layer formed on a substrate with 1 to 10 shots of a pulsed laser beam with a wavelength of 340 to 358 nm and an energy density of 130 to 240 mJ/cm^2 so that said amorphous film is heated and crystallized at a temperature not in excess of the crystalline melting point.

[Claim 2]

A crystalline film production method according to Claim 1, wherein said pulsed laser beam heats said amorphous film either at a temperature not in excess of amorphous melting point or at a temperature above said amorphous melting point and not in excess of the crystalline melting point.

[Claim 3]

A crystalline film production method according to Claim 1 or 2, wherein said crystallization is performed up to a degree of crystallinity in the range of 60 to 95%.

[Claim 4]

A crystalline film production method according to in any one of Claims 1 to 3, wherein a pulse width of said pulsed laser beam is in the range of 5 to 100 ns.

[Claim 5]

A crystalline film production method according to in any of Claims 1 to 4, wherein a pulse frequency of said pulsed laser beam is in the range of 6 to 10 kHz.

[Claim 6]

A crystalline film production method according to in any one of Claims 1 to 5, wherein a short axis width of said pulsed laser beam used for irradiation of said amorphous film is 1.0 mm or less.

[Claim 7]

A crystalline film production method according to in any one of Claims 1 to 6, wherein said irradiation is performed with relative scanning of said pulsed laser beam to said amorphous film at a scanning speed of 50 to 1000 mm/sec.

[Claim 8]

A crystalline film production method according to in Claim 7, wherein said pulsed laser beam is shaped by an optical system into a rectangular or linear beam and said scanning is achieved by moving the optical system at a high speed.

[Claim 9]

A crystalline film production method according to in any one of Claims 1 to 8, wherein crystallites with a size of 50 nm or less and free of protrusions are produced by said crystallization.

[Claim 10]

A crystalline film production apparatus comprising a pulsed laser beam source to emit a pulsed laser beam with a wavelength of 340 to 358 nm, an optical system to lead said pulsed laser beam to an amorphous film for irradiation, an attenuator to adjust the attenuation rate of said pulsed laser beam emitted from said pulsed laser beam source so that said laser beam has an energy density of 130 to 240 mJ/cm^2 at the surface of the amorphous film, and a scanning apparatus to move relatively said laser beam to said amorphous film so that overlapping irradiation of said amorphous film with said pulsed laser beam is performed in the range of 1 to 10 shots.

[Claim 11]

A crystalline film production apparatus according to in Claim 10, wherein said pulsed laser beam source emits a pulsed laser beam with a pulse frequency of 6 to 10 kHz.

[Claim 12]

A crystalline film production apparatus according to Claim 10 or 11, wherein said optical system shapes said pulsed laser beam into a rectangular or linear beam, with a short axis width of 1.0 mm or less.

[Claim 13]

A crystalline film production apparatus according to in any one of Claims 10 to 12, wherein said pulsed laser beam source emits a pulsed laser beam with a pulse width of 5 to 100 ns.