Claim: $\mathrm{Pic}(\mathbb{P}^n) \cong \mathbb{Z}$

Proof: Write $\mathbb{P}^n$ as a union of open affine subsets $U_i = \{x_i \neq 0\}$, $0 \leq i \leq n$. Here, the x_i refer to the standard coordinates on $\mathbb{P}^n$. For an open subset U of $\mathbb{P}^n$, the functions on U are ratios of homogeneous polynomials f/g, where g does not vanish on U and $\deg(f) = \deg(g)$. In particular, the ring of functions on U_i equals $\mathbb{C}[\frac{x_j}{x_i}]$, $j \neq i$.

Now, let E be a line bundle of $\mathbb{P}^n$. E is trivializable on each of the U_i, so let $\alpha_i \in \Gamma(U_i, E)$ be a generator. For any open subset V of U_i, the restriction of α_i to V is a generator for $\Gamma(V, E)$, and it should not cause confusion to call this element α_i as well.

So, on $U_0 \cap U_1$, α_0 and α_1 are two generators of $\Gamma(U_0 \cap U_1, E)$, and so we must have $\alpha_1 = k\alpha_0$, where k is an invertible element of $\mathcal{O}(U_0 \cap U_1) = \mathbb{C}[\frac{x_0}{x_1}, \frac{x_1}{x_0}, \frac{x_2}{x_0}, \ldots, \frac{x_n}{x_0}]$. It is clear that the only invertible elements are of the form $z(\frac{x_0}{x_1})^{d_1}$, where $z \in \mathbb{C}^\times$ and $d_1 \in \mathbb{Z}$. Replacing α_1 with α_1/z, we have $\alpha_1 = (\frac{x_1}{x_0})^{d_1}\alpha_0$.

Repeating this analysis, we must have $\alpha_i = (\frac{x_i}{x_0})^{d_i}\alpha_0$, for $i = 1, 2, \ldots, n$, and integers $d_i \in \mathbb{Z}$. It is clear that E is determined by the d_i. Conversely, the d_i are determined by E, because the only invertible elements ("gauge transformations") on each of the $\mathcal{O}(U_i)$ are scalars. Our next step is to show that all d_i must be equal. Indeed, pick $i \neq j \neq 0$. By the same analysis as before we must have $\alpha_i = z(\frac{x_i}{x_j})^m\alpha_j$ for some $z \in \mathbb{C}^\times$ and $m \in \mathbb{Z}$. But then:

$$\alpha_i = z\left(\frac{x_i}{x_j}\right)^m \alpha_j = z\left(\frac{x_i}{x_j}\right)^m \left(\frac{x_j}{x_0}\right)^{d_j} \alpha_0 = z\left(\frac{x_i}{x_j}\right)^m \left(\frac{x_j}{x_0}\right)^{d_j} \left(\frac{x_0}{x_i}\right)^{d_i} \alpha_i$$

And so we must have $z = 1$ and $m = d_j = d_i$. In fact, this shows that $\alpha_i = (\frac{x_i}{x_j})^d\alpha_j$ for all i, j, and for some fixed integer n. Then, letting E correspond to d, we have a bijection between $\mathrm{Pic}(\mathbb{P}^n)$ and $\mathbb{Z}$. To see that this is a homomorphism: Observe that if E and E' are two line bundles that have generators α_i of $\Gamma(U_i, E)$ and associated integer d (resp. α_i', $\Gamma(U_i, E')$, d'), then $E \otimes E'$ have generators $\alpha_i \otimes \alpha_i'$ on $\Gamma(U_i, E \otimes E')$. Then on, say, $U_0 \cap U_1$ we have $\alpha_1 \otimes \alpha_1' = ((\frac{x_1}{x_0})^d\alpha_0) \otimes ((\frac{x_1}{x_0})^{d'}\alpha_0') = (\frac{x_1}{x_0})^{d+d'}(\alpha_0 \otimes \alpha_0')$.

$\square$

Remark: There are exactly two ways of constructing an isomorphism of $\mathrm{Pic}(\mathbb{P}^n)$ with $\mathbb{Z}$. The standard choice is to assign the integer d to the line bundle, denoted by $\mathcal{O}_{\mathbb{P}^n}(d)$, where for $U \subset \mathbb{P}^n$ open: $\mathcal{O}_{\mathbb{P}^n}(d)(U) = \{f/g \mid f, g \text{ homo.}, g \neq 0 \text{ on } U, \deg(f) - \deg(g) = d\}$. For $E = \mathcal{O}_{\mathbb{P}^n}(1)$, a generator for $\Gamma(U_0, E)$ is $\alpha_0 = x_0$, while a generator for $\Gamma(U_1, E)$ is $\alpha_1 = x_1$. So $\alpha_1 = (\frac{x_1}{x_0})\alpha_0$, and so the description in the proof above would also assign the number 1 to E.